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A

THEORETICAL AND PRACTICAL TREATISE

ON THE

MANUFACTURE

OF

SULPHURIC ACID AND ALKALI,

WITH THE

COLLATERAL BRANCHES.

BY

GEORGE LUNGE, PH.D.,
PROFESSOR OF TECHNICAL CHEMISTRY AT THE FEDERAL POLYTECHNIC SCHOOL, ZURICH.
(FORMERLY MANAGER OF THE TYNE ALKALI-WORKS, SOUTH SHIELDS.)

THIRD EDITION, REVISED AND ENLARGED.

VOLUME I.—PART I.

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PREFACE.

The Second Edition of Vol. I. of 'Sulphuric Acid and Alkali,' embracing the Manufacture of Sulphuric Acid, appeared in 1891, but a copious Appendix at the end of Vol. III. brought the subject down to 1896. It might perhaps appear somewhat early to publish another edition of such a voluminous treatise [*], but the first glance at this book will prove that there was sufficient cause for such a proceeding. Not merely the enormous development of the manufacture of sulphuric anhydride and even of sulphuric acid itself by the contact-process required an altogether new treatment of the subject, but also the vitriol-chamber process with all its ramifications, which in all probability will yield the principal portion of ordinary sulphuric acid for many years to come, has experienced so many changes and improvements that its description ought to be once more brought up to date.

A mere compilation of the voluminous literature of the subject, of patent specifications, and so forth, even combined with frequent visits to acid-works, would not have achieved my purpose—to furnish chemical manufacturers with a trustworthy guide for actual practice, as well as exhaustive scientific and technological information for all students of this branch of industry. But fortunately I have been able to enlist for this edition, like its predecessors, the co-operation of a large number of experienced practical acid-

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[*] It is not intended to publish a third edition of Vols. II. and III. for some time to come.

manufacturers who are far-seeing and large-hearted enough to place their knowledge at my disposal for this book, and therefore for everybody in a similar position, without giving way to the somewhat narrow-minded apprehension that by enlightening their neighbours they might injure their own interests. This sentiment has certainly not been universal. The great acid-trusts in several countries do not give any information, even on such apparently trivial matters as statistics. On the other hand, the United States Census Bulletin, No. 210, compiled by Messrs. Munroe and Chatard, and issued in June 1902, contains much that is welcome to all practical men, over and above the completest and most carefully worked out statistics ever published in that line.

If a jealous restriction of experience within the precincts of one's own business circle were really practised in all cases, it would be a very bad thing, not merely for the cause of technology and therewith of technical progress in general, but even for the largest and most potent manufacturers, who, after all, are not all-powerful or omniscient. But that such a spirit is fortunately far from universal, is best proved by the possibility of compiling a book like the present.

For the *lead-chamber process* I have received (irrespective of a number of smaller notes) valuable remarks or long communications from the following gentlemen or firms, to whom my best thanks are herewith publicly tendered * :—

F. Benker, 129 Rue Martre, Clichy, Paris; Dr. Bräuning, Manager of the Government Works at Oker; G. E. Davis, 32 Blackfriars Street, Manchester; The Royal Saxon Government Works, Muldenerhütte, Freiberg; Herman Frasch, Cleveland, Ohio; W. C. Heraeus, Hanau; L. Kessler, Clermont-

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* This refers merely to the third edition; the names of those who rendered similar services to me in the previous editions are not repeated here.

Ferrand; Dr. G. Krell, Hüsten-Bruchhausen (Westphalia); Metallurgische Gesellschaft, Frankfurt-a.-M.; H. H. Niedenführ, 3 Friedrich-Wilhelmstrasse, Berlin N.; Chemische Fabrik Rhenania, Stolberg (through the late Dr. R. Hasenclever); Dr. A. Zanner (Brussels).

So far as the *contact-process* is concerned, I have been enabled through the special communications of nearly all those who have been mainly instrumental in developing it, especially of the large firms concerned, to completely elucidate, for the first time, the history of this branch of industry which has now acquired such great proportions, and to describe its present state so far as this is compatible with business interests. A host of hitherto unknown facts is contained in the communications of Dr. Arndt, Dr. Jacob, Dr. Krauss (Höchst), Dr. Messel, Monsieur Meunier-Dollfus, Dr. Rabe, Dr. Schroeder, Verein chemischer Fabriken in Mannheim, and Professor Clemens Winkler. The Badische Anilin- und Sodafabrik had already allowed Dr. Knietsch to publish a great number of interesting facts in his celebrated lecture delivered before the Berlin Chemical Society, and that firm has favoured me also with new valuable information for this book.

All contributions to this book by other persons are acknowledged as such in their proper places.

The mass of material thus placed at my disposal would have swelled this book to an altogether inconvenient size, if I had not made some room by cutting out part of the former contents. When preparing this third edition, I adopted the same plan as in the second edition—shortening many descriptions and discussions and entirely omitting others, also making innumerable alterations in details and rewriting whole chapters. But all the more important omissions of this kind are pointed out in the text with reference to the former editions, so that the reader of this third edition is always made aware of the existence of older materials. This seems the proper course for a work of this kind, whose object, among others, is to be of service to inventors as a book of reference, to show them what has been previously done in the field, and thus, on the one hand, to suggest to them ideas for further improvements, and, on the other hand, to spare them disappointments in patent matters. Some, indeed, will miss in this edition various items contained in its predecessors, whilst others may think that I ought to have restricted myself to a description of such materials and apparatus as are still in use, and of such views as are now prevalent. It will never be possible to supply each reader with everything, and *only* everything, he happens to require; I had to content myself with taking a middle course.

In this edition I have not scrupled to replace even valuable and voluminous illustrations by new ones, where I was able to obtain the most recent descriptions. No doubt some readers will miss, for example, the splendid drawings of Schaffner's shelf-burner, from which hundreds of such burners have been erected, but I thought it a waste of space to give these again, along with the new drawings by Niedenführ. In the same way I have sacrificed my own drawings of the Glover tower, of the vitriol-chambers, and many others. Those who wish to consult them will find the former editions referred to in the respective places. A copious index will facilitate the use of this book.

It is now twenty-four years since the first edition of this volume saw the light. The two former editions have earned for the author every commendation he could desire, and more than he honestly could have claimed for himself. It will not, I hope, be thought egotistic if I say that hardly anybody is better able to appreciate the weak sides of this work than its author. Errors, omissions, matters of questionable value will be found by the expert reader here and there. This third edition is still very far removed from the ideal of such a treatise as it exists in the mind of the author. But nobody can do more than is in his power, and such readers as know (or think they know) this or that thing better, and who may be inclined to sharp criticism, had best ask themselves the question whether *they* would come up to the ideal if they had to write such a book, and whether they cannot derive some valuable information even from this imperfect performance, which probably represents the last opportunity the author will have of treating the subject.

Zurich, August 6th, 1903.

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ADDENDA.

FIRST BOOK.

SULPHURIC ACID.

INTRODUCTION.

Formerly the term "alkali manufacture" nearly always comprised a cycle of operations, beginning with the manufacture of sulphuric acid and proceeding to that of sulphate of soda (salt-cake), hydrochloric acid, soda-ash (with caustic soda, soda-crystals, &c.), and bleaching-powder. This cycle is not completed in all factories, but frequently (at the present day even more so than formerly) the operation stops at sulphuric acid or sulphate of soda; but we may embrace all this under the general term of "Sulphuric Acid and Alkali Manufacture."

In this wider meaning the products of alkali-making are necessary materials for many metallurgical processes, for the manufacture of artificial manures, soap, fatty and mineral oils, glass, paper, many inorganic and organic colouring-matters (especially nearly all coal-tar dyes), and even of many articles of food,—that is to say, for nearly all branches of manufacturing chemistry. In fact, among all branches of chemical industry the cycle of technical operations connected with alkali-making is preeminent, not merely from the magnitude of the works and the absolute bulk of the raw material used and the quantity produced, but also from the fact that most other chemical products require one or more branches of alkali-making as the conditions of their own existence. It can be truly said that the manufacture of acids and alkali is the foundation upon which the whole chemical industry of our times is built up, and that such industry cannot be much developed in any country not possessing a flourishing alkali trade, or not being at least specially well situated for buying the produce of the latter. It is thus evident how great is the importance of the alkali trade in its wider meaning to the civilization of mankind, though we should certainly be going too far if we measured, as some have done, the civilization of a country by the development of this special industry.

Formerly the whole cycle of processes here described was intimately connected with the great invention of Leblanc, now rather more than a century old. Twenty years ago, although the ammonia-soda process had then already more than proved its right to be considered a full success, it had not yet shaken in any tangible degree the supremacy of the Leblanc process, at least not in Great Britain. In the latter process the different branches of "alkali-making" mentioned above are connected in such a manner that only under special local conditions can one or more of the principal substances be omitted. Formerly this was the case even less than now, as the competition of ammonia-soda ash has completely altered some of the conditions of trade, making it unremunerative in many cases to convert the sulphate of soda into the carbonate. Thus there exist now many works stopping at the manufacture of sulphuric acid, and others which go as far as sulphate of soda, together with chlorine products; but very many proceed still further, going on to the manufacture of soda in its various branches.

The manufacture of *sulphuric acid* is in reality a very large industry, quite apart from its connection with the Leblanc process. Enormous quantities of it are required for the manufacture of artificial manures (fertilizers), and therefore every large manure factory makes its own sulphuric acid. This is done also by the largest sulphate-of-ammonia works, petroleum refiners, coal-tar dye manufacturers, and in a few other cases. Some works in England, and many on the Continent, make sulphuric acid to a great extent, or even entirely, not for their own use, but for sale. Since this acid is no longer sent out in any considerable quantity in glass carboys, but in iron tank-waggons, it can be carried to considerable distances at moderate cost.

As sulphuric acid is mostly made from pyrites, its manufacture is intimately connected with the recovery of *copper* from the cinders, in which process iron oxide, silver, and other by-products are obtained.

A very large (formerly even the largest) quantity of sulphuric acid is used up at the works themselves for the manufacture of *sulphate of soda* (*salt-cake*) and *sulphate of potash*, in which *hydrochloric acid* is a necessary by-product. Sometimes salt-cake is obtained without previously manufacturing sulphuric acid, as a by-product of other manufactures or by the "direct process" of Hargreaves and Robinson. There is only one use of salt-cake on a large scale, except for alkali-making, namely, for the manufacture of glass; but a much larger quantity of salt-cake still enters into the *Leblanc process for manufacturing soda.* This article is mostly the final product, either in the calcined or crystallized or caustic state, and the series of operations is thus brought to a close in this direction.

Hydrochloric acid (*muriatic acid*) is, of course, sold as such to some extent, but in nothing like such large quantities as sulphuric acid, as its carriage is impossible in metallic vessels, and therefore more expensive and troublesome. Most of it is at once, sometimes even without condensation to liquid acid, converted into *chlorine*, which, being a gas, is immediately worked up into bleaching-powder or chlorate of potash, or occasionally into other products; a comparatively small quantity of it is sold in the state of liquid chlorine. The time when the hydrochloric acid was condensed merely to satisfy the exigencies of laws made for protecting the health and vegetation of a neighbourhood, and was then run to waste into the nearest watercourse, is now past, since the process of decomposing salt by sulphuric acid is only profitable if the hydrochloric acid is fully utilized: this acid has thus risen from the rank of a by-product to that of the best-paying principal product.

Once more the conditions of the Leblanc process were changed by the solution of the problem of the *recovery of sulphur* from the alkali waste, and it has now been made into a real cycle, into which common salt and coal enter at one end, alkali and chlorine issuing at the other, whilst sulphur and possibly even lime are made to do service over and over again. This, however, appears most clearly in Vols. II. & III. of this Treatise; to which we also refer for such general observations as the ammonia process of soda manufacture calls for.

CHAPTER I.

HISTORICAL AND GENERAL NOTES ON THE MANUFACTURE OF SULPHURIC ACID.

History of the Manufacture of Sulphuric Acid.

ACCORDING to Rodwell ('Birth of Chemistry') it is very probable that sulphuric acid was already known to the ancients; but usually its first, although indistinct, mention is ascribed to the Arab Geber, who speaks of the "spirit" which can be expelled from alum and which possesses solvent powers. Geber is, however, a mythical personage, and many of his alleged numerous discoveries have wrongfully crept into the Latin "translations" of his pretended writings, as proved by Berthelot and Steinschneider (comp. Lippmann, Zsch. angew. Chem. 1901, p. 646), who show that sulphuric acid was unknown to Arabian writers about 975 A.D. Others give the honour of its discovery to the Persian alchemist Abu-Bekr-Alrhases, who is said to have died in 940. Vincentius de Beauvais (about 1250) alludes to it; and Albertus Magnus (1193–1280) speaks of a *spiritus vitrioli Romani*, which can only have been sulphuric acid; his "sulphur philosophorum" is the same thing.

With all distinctness Basilius Valentinus, in his 'Revelation of the Hidden Manipulations,' describes its preparation from calcined copperas and silica, and, in his 'Triumphal Car of Antimony,' also its preparation by burning sulphur with saltpetre (Kopp, 'Geschichte der Chemie,' iii. p. 303); but he took the two to be different substances.

Gerhard Dornæus (1570) described its properties accurately; Libavius (1595) recognized the identity of the acids from different processes of preparation; the same was done by Angelus Sala (1613), who pointed out the fact, which had sunk into oblivion since Basilius, that sulphuric acid can be obtained by burning sulphur in moist vessels (of course with access of air); after that time it was prepared by the apothecaries in this way. An essential improvement, viz. the addition of a little saltpetre, was introduced in 1666 by Nicolas le Fèvre and Nicolas Lémery. This caused a sort of manufacture of vitriol which is said to have been introduced into England by Cornelius Drebbel: this only is certain—that a quack doctor of the name of Ward first carried on sulphuric-acid making on a large scale at Richmond near London, probably a little before 1740. Ward employed large glass vessels up to 66 gallons capacity, which stood in two rows in a sand-bath, and which were provided with horizontally projecting necks; at the bottom they contained a little water. In each neck there was an earthenware pot, and on this a small red-hot iron dish, into which a mixture of one part saltpetre and eight parts of brimstone were put; then the neck of the bottle was closed with a wooden plug; on the combustion being finished, fresh air was allowed to enter the vessel, and the operation was repeated till the acid had become strong enough to pay for concentrating in glass retorts.

Ward called the product "oil of vitriol made by the bell" (already Basilius Valentinus had used the expression "per campanam" in this sense), in order to distinguish the spirit of vitriol made from brimstone from that distilled from sulphate of iron, the latter having been made on a kind of manufacturing scale in England previously: an exact description of this is given by J. C. Bernhardt in his 'Chemische Versuche und Erfahrungen,' 1755. Ward's process, troublesome as it is, reduced the price of the acid from 2*s*. 6*d*. per ounce (the price of the acid from copperas or from burning brimstone under a moist glass jar) to 2*s*. per lb.

An extremely important improvement in this process was the introduction of the *lead chambers*, which by general consent is ascribed to a Dr. Roebuck of Birmingham, who in 1746 erected such a chamber 6 feet square, and in 1749, in partnership with Mr. Garbett, built a factory, founded thereon, at Prestonpans in Scotland, in order to supply acid for the bleaching of linen. The mixture of brimstone and saltpetre in the above proportion was put into small iron waggons which were run into the chamber on a railway: the chamber was closed, and the process carried on intermittently in this way. Guttmann (Journ. Soc. Chem. Ind. 1901, p. 5) gives a detailed description and some drawings of such "lead-houses" and their style of working from a manuscript by a Birmingham chemist, W. E. Sheffield, written between 1771 and 1790. The cost of acid of spec. grav. 1·844 per ton was £22 6*s*. 4*d*. without labour.

Soon other works followed at Bridgenorth, and at Dowles in Worcestershire, where the chambers were already made 10 feet square; in 1772 a factory was erected in London with 71 cylindrical lead chambers, each 6 feet in diameter and 6 feet high. In 1797 there were already six or eight works in Glasgow alone. According to the statements given in Mactear's 'Report of the Alkali and Bleaching-Powder Manufacture in the Glasgow District' (p. 8), the acid at that time cost the Glasgow manufacturers £32 per ton, and was sold at £54. At Radcliffe, near Manchester, it cost, in 1799, £21 10*s*. per ton, without interest on capital. In the latter place there were six chambers 12 feet long, 12 feet wide, and 10 feet high, with roofs like those of houses, and valves opened between each operation; on their bottom were 8 or 9 inches of water; every four hours a mixture of 1 lb. saltpetre and 7 lb. brimstone was burnt in each chamber on iron shelves, of which each chamber contained four, 4 inches distant one from another. The shelves were made of very thin iron, in order to get heated very quickly, and rested on iron frames, by means of which they could be slid in and out; a quarter of an hour before each operation the valves and doors were opened in order to allow air to enter. Thus, weekly, 1386 lb. of brimstone and 198 lb. of saltpetre were burnt, yielding 1800 lb. of oil of vitriol—that is, 130 per cent. of the sulphur with a consumption of 14·28 per cent. saltpetre on the same. In six weeks the strength of the acid attained only 1·250 sp. gr.; it was thus run off and concentrated up to 1·375 sp. gr., in which state it was used and sold. At Prestonpans, in 1800, a yield of only 111 per cent. on the sulphur was attained, with a consumption of 13 per cent. saltpetre on the brimstone; in 1813 there were in that place 108 chambers of 14 feet length, 10 feet height, and 4½ feet width. In 1805 there existed at Burntisland a factory with 360 chambers of a capacity of 19 cubic feet each. R. Forbes Carpenter and W. F. Reid also give some interesting notes on the early manufacture of sulphuric acid (Journ. Soc. Chem. Ind. 1901, p. 7). The former mentions acid-chambers erected in Cornwall from dressed granite, with lead top and bottom.

In the meantime the first lead chamber in France had been erected at Rouen by Holker in 1766. In 1774, in that place, on the advice of De la Follie, an important improvement was introduced, viz. the introduction of steam into the chambers during the combustion of brimstone. In 1793 Clément and Desormes showed that the acid-chambers can be fed by a *continuous* current of air, by which a great deal of saltpetre could be saved. They showed that the oxidation of sulphurous acid takes place to the extent of nine tenths at the expense of atmospheric oxygen, and that the saltpetre plays only the part of intermediary between the air and the sulphurous acid. By this the modern theory of the essence of the sulphuric-acid-making process was established; but it took a remarkable long time before the difficulties were overcome which stood in the way of introducing the continuous system into practice. Usually the introduction of the continuous burning of brimstone is ascribed to Jean Holker (a grandson of the first Holker), in 1810; but, according to Mactear, a continuous system had been introduced at St. Rollox, at least partially, already in 1807: steam was first introduced there in 1813 or 1814.

In Germany the first lead chambers seem to have been those at Ringkuhl, near Cassel. One of the oldest chambers was that erected by Dr. Richard at Potschappel near Dresden in 1820; as he had no plumber at his disposal, he had to solder the chamber himself with soft solder and a smoothing-iron (Bode, in his translation of H. A. Smith's 'Sulphuric Acid Manufacture,' p. 96). This chamber was still charged intermittently, 100 lb. of brimstone yielding only 150 lb. of vitriol.

Lampadius, in a treatise published in 1815 *, speaking of sulphuric acid as then made in England and at Schwemsal near Leipzig, describes the lead chambers as "rooms," about 25 feet square with a stone floor, lined throughout with lead, with two doors through which sulphur is introduced and burned on iron dishes, holding ½ cwt. of brimstone, mixed with 20 per cent. nitrate of potash, steam being introduced from a copper outside the room. Through four pipes and taps, during the later stages of the combustion (which lasted three hours), a little air was admitted. The "room" was exposed to great strain through the

---

* Quoted by Cl. Winkler, Zsch. angew. Chem. 1900, p. 731. Some of the following statements are also taken from this paper.

strong expansion and subsequent contraction of the atmosphere inside. The dilute acid formed was boiled down in glass retorts to spec. grav. 1·800.

The invention of soldering lead with the same material or "burning" by means of the hydrogen blowpipe is due to Debassayns de Richemond, in 1838. As late as 1846 Prechtl's 'Technical Encyclopædia' (xiv. p. 246) mentions the chamber-sides as being sometimes covered with a crust of chamber-crystals, ½ or 1 inch thick, which proves the want of understanding the process at that time.

Kestner, of Thann in Alsace, was the first to collect the products of condensation at the chamber-sides in order to regulate the working of the chambers thereby. This innovation was at once considered of such importance that Kestner was called to Glasgow in order to introduce his plan into Tennant's works.

In 1827 Gay-Lussac's condensing-apparatus for the nitre-gas escaping from the chambers was invented: at Chauny this apparatus was erected in 1842, at Glasgow in 1844. But we have now come so near the present time that we may conclude the historical part of our task.

General Principles of the Manufacture of Sulphuric Acid.

Sulphuric acid can be obtained on a large scale in one of two ways—viz., first, by burning sulphur or sulphides into sulphur dioxide and further oxidizing the latter, or, secondly, by decomposing natural or artificially prepared sulphates. The latter process, apart from several proposals so far not carried out practically, until quite recently served for making fuming oil of vitriol, which will be treated of hereafter; by far the greater portion of sulphuric acid has always been obtained by the former process, which will occupy us in the first instance. We shall, at first, only describe those apparatus and processes which actually serve for manufacturing on a large scale; and we shall close by mentioning the alterations which have merely remained as proposals, as well as the processes founded on totally new principles.

By the *combustion of sulphur*, either free (as brimstone, gas-sulphur, &c.) or combined with metals or with hydrogen, *sulphur dioxide* (SO_2) is always formed at first. Sulphuretted hydrogen, even when mixed with as much as 70 per cent. of inert gases (nitrogen), can be lighted like illuminating-gas and continues burning without any difficulty, aqueous vapour being formed at the same time as SO_2. Brimstone ignites in the air at a temperature rather below 300° C.; and when once it has begun to burn, the heat generated suffices to raise the whole of the sulphur to the point of ignition, provided that sufficient air be present. A number of metallic sulphides behave similarly: the most important of these for our purpose is the iron disulphide, FeS_2; but here special precautions must be taken, so that the whole mass may be completely burnt (roasted). In both cases, along with sulphur dioxide, SO_2, a little trioxide (sulphuric anhydride), SO_3, is always formed, and, in the presence of water or steam, also sulphuric acid, SO_4H_2, more or less diluted with water. Moreover an aqueous solution of sulphurous acid in contact with air gradually changes into sulphuric acid. In both cases it is, of course, the oxygen of the air which converts the SO_2 into SO_3 or SO_4H_2; but this reaction at the ordinary or only moderately elevated temperature goes on far too slowly to be applicable for technical purposes.

There are two ways of increasing the velocity of the oxidation of sulphur dioxide. One of these, which is principally applicable to dry gases and therefore leads to the preparation of sulphur trioxide in the anhydrous state, is the employment of "catalytic" substances. We shall discuss this in Chapter XI., devoted to the "*Contact processes.*"

The second way, which is exclusively applicable to the production of real sulphuric acid, H_2SO_4, is founded on the property of the acids of nitrogen to serve as carriers of oxygen from atmospheric air upon sulphur dioxide and water, the original nitrogen oxide being always re-formed. This process will be explained in detail when we treat of the theory of the formation of sulphuric acid; it is called the *vitriol-chamber process.*

The reaction between nitrogen acids and sulphur dioxide only goes on in the presence of water; and we must add at once that, in practice, much more water is needed than suffices for the formation of SO_4H_2; the sulphuric acid formed is therefore always *dilute*, and must be *concentrated* for most purposes.

For some purposes the acid must also be deprived of certain foreign substances which get into it from the raw materials and the apparatus; and in such cases the sulphuric acid has to be *purified.*

Thus our subject subdivides itself into the following headings :—

1. An examination of the *raw materials* of the sulphuric-acid manufacture, and an account of the *properties of the oxides and acids of sulphur.*

2. *The generation of sulphur dioxide.* Since the processes differ very much, both as to apparatus and the method of proceeding, we have to distinguish between (*a*) sulphur dioxide from brimstone, (*b*) from metallic sulphides, (*c*) from sulphuretted hydrogen.

3. *The conversion of sulphur dioxide into sulphuric acid* in the so-called vitriol-chambers.

4. The *purification.*

5. The *concentration* of sulphuric acid.

6. The *contact processes.*

7. The *utilization of the by-products.*

CHAPTER II.

THE RAW MATERIALS OF THE SULPHURIC-ACID MANUFACTURE (INCLUDING NITRIC ACID).

1. NATURAL SULPHUR (BRIMSTONE).

BRIMSTONE, owing to its being found in nature in the free state, has been known to mankind since very ancient times. It is hardly necessary to point to its being noticed in the Bible; it is also mentioned several times in the Homeric poems. The Romans evidently obtained it in the same way as is done now, by melting it out of its mixture with marl, &c. The ancients employed it principally for fumigating purposes, both on account of its disinfecting properties and as a religious rite (compare the well-known passage from the Odyssey, where Ulysses purifies his house after slaying the intruders), but also for many of the uses to which it is put at the present day, as for cleaning wine-casks, for destroying fungus-growths in vineyards and orchards, for plasters in skin-diseases, for lighting fires and preparing torches, for cementing glass, for bleaching, for "niello" work on metals *.

In modern times brimstone has been used for most of the just-mentioned purposes and for many others; but we are here concerned only with its use for the manufacture of sulphuric acid. Brimstone is undoubtedly the most convenient raw material for this manufacture, and for a long time all the sulphuric acid of commerce was made from it; but its use in this respect has been almost entirely abandoned in most localities, and is not likely to be revived, since iron-pyrites, and more especially that containing a few per cent. of copper, supplies sulphur for the above purpose far more cheaply than natural brimstone ever can do. In spite of this, brimstone is still a principal raw material for the manufacture of sulphuric acid in America (where, however, it has lost its former

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* I owe these historical notes to a treatise by Professor Blümner, of Zürich in the 'Festschrift zur Begrüssung der Philologen-Versammlung' (Zürich, 1887), p. 23 *et seq.*

exclusive sway), and it is also used to some considerable extent in England for that purpose, but very little indeed in other European countries.

A somewhat considerable quantity of brimstone is also consumed in the manufacture of sulphurous acid, principally in order to prepare bisulphate of lime for the manufacture of wood-pulp.

Sulphur is an element whose atomic weight is now assumed to be 32·06 (oxygen = 16). It is very brittle; its hardness is from 1·5 to 2·5 of the ordinary mineralogical scale; its specific gravity is 2·07. As usually occurring, it is semi-transparent at the edges and of the well-known bright yellow colour, which darkens with an increase of temperature; at −50° it is nearly devoid of colour. Its taste and smell are very slight. It does not conduct electricity, but itself becomes electric by friction; and it is therefore difficult to powder finely, as it adheres to the mórtar and pestle.

Sulphur melts at 111°·5 C., and forms a thin, light-yellow liquid, which, on being more strongly heated, becomes darker and thicker; at 250° to 260° C. it is nearly black, and so viscid that it does not run out when the vessel is upset; at a still higher temperature it becomes thinner again, keeping its brown colour; and at 440° C. it boils, forming a brownish-red vapour; but it begins to volatilize before boiling; and its action on silver seems to show that it does so to a slight extent even at the ordinary temperature (unless there is formation of H_2S in this case).

Sulphur exists in different allotropic conditions. That occurring in nature often appears in rhombic crystals, mostly pointed rhombic octahedra, whose physical properties have been described above; this α-modification is also obtained by crystallizing sulphur from its solution in carbon disulphide. The β-modification is obtained by slowly cooling melted sulphur, and pouring off the liquid portion when another portion has crystallized; it consists of long thin oblique rhombic prisms, belonging to the monoclinohedric system, of a brownish-yellow colour, transparent, spec. grav. 1·982; they gradually pass over into the α-modification, completely so after a few days, even at the ordinary temperature—suddenly by shaking or scratching; the colour then becomes light yellow; and the crystals lose their transparency, but remain as pseudomorphs of the β-sulphur. The sulphur in rolls consists, when fresh, of β-sulphur—after a short time, of α-sulphur. When sulphur has been heated up to the point of viscosity, and is then poured into very cold water, the γ-modification is formed, viz. amorphous, soft, tough, reddish-brown sulphur, of 1·957 spec. grav.; this also is gradually converted into α-sulphur; but it takes some time before this conversion is complete. The tough state lasts very much longer if resinous substances, iodine, &c. are mixed with the sulphur, even in very small quantity. This modification is partly contained in the "flowers" of sulphur.

Heated in the air to 250° C.*, sulphur inflames and burns with a purplish-blue flame, forming sulphur dioxide (SO_2), and giving out 2221 metrical units of heat per gram of sulphur. More exactly, according to Thomsen (Berl. Ber. 1880, p. 959), the heat evolved in burning the different modifications of sulphur, expressed in atomic calories (that is, applied to 32 grams of sulphur), is:—

S (rhombic, octahedric) $+O_2=SO_2=+71{,}080$ cal.
S (monoclinic) . . . $+O_2=SO_2=+71{,}720$ cal.

Hence the conversion of 32 parts by weight of monoclinic into rhombic sulphur is accompanied by the evolution of 640 calories. Berthelot, however (Compt. rend. xc. p. 1419), states the figure for octahedric sulphur $=+69260$ atom. cal. $=2164$ gram-calories.

Hydrogen combines with sulphur very slightly at a temperature of 120°, very sensibly so at 200°. On boiling sulphur with water, hydrogen sulphide is evolved and sulphuric acid is found in the residue (Cross & Higgin, J. Chem. Soc. xxxv. p. 249; comp. also Colson, Bull. Soc. Chim. [2] xxxiv. p. 66; Böhm, Jahresb. 1883, p. 225).

Sulphur is insoluble in water, a very little soluble in alcohol and in glycerine, rather more so in essential oils, but easily soluble (excepting the γ-modification) in disulphide of carbon and in chloride of sulphur.

The sulphur occurring in commerce as *refined sulphur,* in rolls or as "rock-sulphur," is frequently almost chemically pure. "Flowers of sulphur" always contains a little sulphurous acid, also some sulphuric acid, persistently retained in spite of prolonged washing; it owes its greater efficacy against diseases of the vine (oïdium) and other cases principally to this property.

O. Roessler (Arch. d. Pharm. 1887, p. 845) states that sulphur in rolls is practically free from acids of any sort. Flowers of sulphur contains a somewhat considerable quantity of sulphurous

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* Comp. J. R. Hill, Chem. News, 1890, lxi. p. 126.

acid (100 grams up to 3·14 c.c. of SO_2), which may be partially oxidized to sulphuric acid ; thiosulphuric acid is not found in it, but in milk of sulphur (up to 0·15 per cent.).

Natural Occurrence of Sulphur.

Sulphur occurs in nature in very large quantities, both in the free state and in combination with other bodies as sulphides and sulphates. Deposits of sulphur are forming at the present day, especially in volcanic countries, by the decomposition of sulphuretted hydrogen and of sulphurous acid.

Daubrée (Compt. rend. xcii. p. 101) noticed a recent formation of sulphur in the subsoil of Paris, from the action of organic substances on sulphates ; and the same action has been observed in many mineral springs, where it is especially attributed to the action of Algæ, such as *Beggiatoa, Oscillaria*, and *Ulothrix* (Compt. rend. xcv. pp. 846 & 1363).

But of far more consequence are the beds of sulphur deposited in former geological periods. The most important of all are those of Sicily, in the chalk ; next, those in the Romagna and in other parts of Italy. The *Sicilian sulphur industry* is described in detail by Angelo Barbaglia in Hofmann's Official Report on the Vienna Exhibition, i. p. 144, and by Parodi (Berichte d. deutsch. chem. Ges. 1874, p. 358). According to the latter, the disposable stock of sulphur in Sicily is said to amount to ten millions of tons ; so that it would be exhausted about 1950. Other calculations gave more than twice that amount. The apparatus for melting the sulphur out of the "sulphur-earth" in Sicily is also described by Barbaglia.

Further descriptions of the Sicilian sulphur industry are found in the 'Chemiker-Zeitung' of 1882, pp. 1389, 1405, 1421 ; also in 'Zeitsch. f. angew. Chemie,' 1890, p. 56, in the 'Journal of the Society of Chemical Industry,' 1890, p. 118 ; by Bechhold, 'Zsch. angw. Ch.' 1894, p. 33 ; by Frank, *ibid.* 1900, p. 843 ; by Inngfleisch (Monat. Scient. 1901, p. 511).

Probably the most exhaustive description of the modern Italian sulphur industry is that given by Aichino, in 'Mineral Industry,' viii. p. 592.

Here we quote only a few brief notes on more recent processes or proposals for extracting sulphur from its ores (whether intended for Sicilian sulphur or that from other localities).

In recent years the "Gill kilns" have rapidly gained ground in replacing the calcarone methods, and they increase the output of sulphur by 50 per cent. These kilns consist of an oven covered by a cupola, called a "cell;" inside there is a smaller cupola, within which a coke fire is burning. Each cell holds from 5 to 30 cubic metres of ore. There are generally six cells working in an angular battery. The gases generated in the first cell pass by lateral channels into the next; by the time the fusion is completed in the first cell, the contents of the second cell are already heated up to the igniting-point by the gases, and so on. The gases heavily charged with sulphur are not lost as in the calcarone method; the yield is much larger, the time shorter (three or four days for each cell), and as the quantity of smoke is much less, the work can be continued almost all the year round without danger to the crops. In 1888 there were only 365 cells in 40 mines, in 1894 the number had increased to 1821 cells in 225 mines, that is over two-thirds of the total.

E. F. White (Eng. Min. Journ. lxii. p. 536) extracts sulphur from sulphur-ores by passing the latter downwards between two conical steam-heated vessels, where the sulphur is fused and runs out at the bottom.

De la Tour de Breuil (Compt. rend. xciii. p. 456) employs a 66-per-cent. solution of calcium chloride for the same purpose. C. Vincent recommends this process (Bull. Soc. Chim. xl. p. 528).

K. Walter, in Milan, has patented an apparatus for continuously melting out sulphur by combustion of part of the sulphur itself, and converting the sulphur dioxide formed into sulphuric acid in lead chambers (Chem. Zeit. 1886, p. 1199).

The American patents of F. Dickert, Nos. 298,734 and 301,222, describe an apparatus for melting sulphur, consisting of a jacketed pan connected by a perforated diaphragm with another jacketed pan turned bottom upwards. The melting is produced by means of steam introduced into the jacket.

Very ingenious is the process of Herman Frasch (U.S. pat. 461429, 461430, 461431 of 1891), which is applied to the Louisiana sulphur, where quicksand makes it impossible to use the ordinary methods. A well is sunk by drilling in the same way as for petroleum. This well is cased with an iron pipe 10 in. in diameter, reaching 10 feet into the rock overlying the sulphur-bed. Inside this there is a 6-in. pipe, inside the latter a 3-in. pipe, and, finally, in the centre a 1-in. pipe. The well is carried down to the bottom of the sulphur-bed, and the 6-in. pipe and smaller pipes are dropped nearly to the bottom of the lode. Water heated to 166° C. is forced down the 10-in. and 6-in. pipes under corresponding pressures, and on coming in contact with the sulphur it is melted and collects in the well. Ordinary pumping not having answered, compressed air is forced down through the 1-in. pipe, which mixes with the molten sulphur and reduces its specific gravity so that it rises in the 3-in. pipe to the top with great rapidity. As much as 150 tons of sulphur has been pumped in 24 hours. About 50 tons of coal per day are burned under the boilers.

The loss of heat is, of course, very great, and there is an uncertainty about the way in which the impurities present may choke up the pipes. In 1896 one hole, sunk in very pure sulphur, produced 2100 tons; this was continued in 1898, bringing up the total to 4509 tons. However, according to vol. vii. of 'Mineral Industry,' p. 643, in 1898 the conclusion was reached that the process was unprofitable; but this is entirely wrong. In February 1902 I received from the inventor (Mr. Frasch) a set of photographs, taken on the spot a few weeks before, exhibiting the manufacture on a large scale, the pumps discharging a full 3-in. stream of liquid sulphur all through. The boiler-power is being increased from 2100 to 4300 H.P. With the present (lower) power the average production is 100 tons per day from one well; up to 250 tons per day has been realized before. The liquid sulphur is discharged into bins up to a size of 72 ft. × 60 ft. × 5 ft., where it solidifies and is broken up for shipment. Many thousand tons have been pumped and shipped, and there are large stocks on hand shown in those bins.

Analyses of Sicilian sulphur (Mène, Monit. Scient. 1867, p. 400):—

Sulphur soluble in CS_2	96·2	92·1	92·1	91·3	90·1	90·0	88·7
Sulphur insoluble in CS_2	...	...	...	1·5	2·0	2·1	1·7
Carbonaceous matter	0·5	1·0	1·1	0·7	1·0	1·1	1·0
Sand	1·5	2·3	2·8	3·3	2·3	2·8	5·5
Limestone and strontium sulphate	1·8	4·1	3·0	2·5	4·1	3·0	2·8
	100·00	99·5	99·0	99·3	99·5	99·0	99·7

[Mène's samples are evidently of a very low quality.]

The average price of sulphur in Sicily in 1881 was 115 lire, in 1882 105 lire, in 1887 only 69 lire (say £2 15*s.*) per ton.

A Report by the Italian Minister of Agriculture for the year 1894 (Chem. Ind. 1895, p. 182) describes the depressed state of the Sicilian sulphur industry.

In 1896, by the formation of the Anglo-Sicilian Sulphur Company, working with English capital, the Sicilian sulphur industry was at last placed on an economically sound basis, and at the same time the ruinous cutting down of prices ceased. During 1900 the average price for "best thirds" was £3 13*s.* 6*d.* per ton f.o.b. Catania.

The total exportation of sulphur in Sicily during the year ending June 30, 1900, was 517,741 tons; during the year ending June 30, 1901, 521,497 tons. This quantity was exported to different countries as follows:—

	1900-1901. Tons.	1899-1900. Tons.
United States	147,094	138,846
France	98,455	98,393
Italy	85,210	101,624
Germany	30,549	26,290
Norway, Sweden, Denmark	27,373	18,313
Greece and Turkey	22,304	19,795
Great Britain	19,923	25,933
Russia	19,878	16,815
Austria	19,647	23,067
Holland	15,813	11,781
Portugal	11,315	11,462
Belgium	9,316	8,845
Spain	3,566	6,298
Other countries	11,059	10,259

(The quantities for a number of years previously to the above are given in our second edition.)

Northern Italy formerly yielded a very large quantity of brimstone, especially the Romagna; but many of the beds are now exhausted, and the production is slowly receding, from 23,274 tons in 1886 to 21,663 tons in 1887 (details in the Chem. Zeit. xii. p. 1659; abstr. J. Soc. Ch. Ind. 1889, p. 142). The whole of this brimstone is used for inland consumption, as a remedy against the vine-disease.

Sulphur containing *selenium* is found in the Lipari Islands and near Naples, but not in quantity.

In many other parts of the world deposits of sulphur have been found, and have been sometimes declared to be very important; but hitherto these sulphur-mines have not made any sensible impression on the sulphur trade, of which Sicily has still almost the monopoly. The more important of these sulphur-mines are the following:—

Andalusia produces sulphur, some of which is refined in Almeria.

In *Germany* sulphur has been found at Stassfurt (Berl. Ber. 1890, p. 192) and in Upper Silesia, near Ratibor, where beds up to 20 ft. thick exist (Chem. Ind. ii. p. 136; Fischer's Jahresb. 1882, p. 223). It has been worked by extracting it from the ore by means of carbon disulphide.

The production of sulphur in Germany, as indicated by the official statistics, does not distinguish between natural sulphur and that which is recovered in the Leblanc process. It amounted in 1897 to 2317 tons, in 1898 to 1954 tons, in 1899 to 1663 tons.

In 1899 the importation was 31,196 tons, in 1900 40,689 tons. The exportation is very small.

In *Austria*, at Swoscowice near Cracow, an old sulphur-mine exists which for some years was carried on with great vigour, the sulphur being extracted from the marl by means of carbon disulphide. This bed is now practically exhausted, and the mine has ceased working (Wagner's Jahresb. 1878, p. 333, 1879, p. 272; Fischer's Jahresb. 1885, p. 204).

Russia possesses considerable stores of sulphur. A bed of brimstone has been found by Gluschkoff in the Astrachan Government, on the east bank of the Baskuntschak salt-sea; it is a mixture of sandy rock with 30 to 35 per cent. of pure sulphur (Fischer's Jahresb. 1884, p. 264). In West Siberia considerable beds of sulphur are said to exist. In the Vistula district a sulphur-bed is being worked at Czarki, which in 1883 yielded 60,000 pud. In the sandy steppe of Karakum a large number of conical hills have been discovered consisting of sulphury rock of 50 per cent. (Chem. Zeit. 1884, p. 478). In the north of the Caucasus, in the Grodno district, sulphur has been found by

Baron Heyking (Chem. Zeit. 1887, p. 1620). According to Chem. Ind. 1892, p. 443, the sulphur is obtained at Tschirkat in Daghestan to the extent of 300,000 pud (at 40 lbs.) per annum; the selling price is 1·18 roubles per pud.

According to Chem. Zeit. 1894, p. 2002, a large bed of brimstone has been found in Transcaspia, 60 versts from the port of Usun-Ada on the Caspian Sea, only 2 versts from a railway-line. The bed is just below the surface of the ground and is worked by open quarrying. The ore contains from 35 to 40 per cent. sulphur, and costs 20 to 25 copeks at Usun-Ada. If the results expected were realized, Russia would become entirely independent of Sicilian sulphur. Possibly this is the same occurrence which is reported in Journ. Soc. Chem. Ind. 1900, p. 867, as "the richest in the world," 100 miles from Khiva, extending over 23 square miles.

Chonski (Chem. Zeit. 1895, Repert. p. 411) reports on the production of sulphur, which, he says, has been tried in several places in Russia, but has been everywhere discontinued. He enumerates the drawbacks connected with the various methods for extracting sulphur from the raw ore. This paper should be consulted by those who consider any newly discovered vein of sulphur-ore as being equal to ready money.

Comp. on Russian brimstone also Zsch. angew. Chem. 1897, p. 36; Chem. Ind. 1898, p. 241; Niedenführ, Chem. Zeit. 1897, No. 30; Machalski, Engin. Min. Journ. lxx. p. 216; Chem. Trade Journal, 1900, xxvii. p. 220.

Brimstone is got near Mossul in *Mesopotamia,* near *Cairo,* and in *Tunis.* At Djemsah and Ranga, on the coast of the *Red Sea,* the "Compagnie Soufrière" is said to get 300 tons monthly.

Very large quantities of sulphur are said to exist in *Iceland,* even more important than those in Sicily; the deposits at Guldbringe Syssel, in the south-west of Iceland, were some time ago at work with satisfactory results (Chem. News, xl. p. 31).

Japan possesses very large stores of sulphur, but the absence of facilities for increasing its output and for shipping it has hitherto very much restricted the development of the sulphur industry in that country. Formerly (comp. J. Soc. Chem. Ind. 1890, p. 344) there was only one place where sulphur was worked on any scale, namely Atosanobori, near Kushiro, on the south-east coast of the island in which the port of Hakodate is situated.

The Atosanobori mine is part of an extinct volcano, whose crater and slopes are partially covered with a 50-per-cent. sulphur-ore. According to the lowest estimate this mine contains a million tons of good ore, but there is probably five times as much. The output is at present about 9000 tons per annum; the cost of the sulphur free on board at Kushiro is about 30*s*. 10*d*., but it has hitherto been shipped from Hakodate, where it costs £2 3*s*. 2*d*. per ton, which is not remunerative. The exportation was 1541 tons in 1885, 4972 tons in 1886, 7096 tons in 1887, 3609 tons in 1888, 15,700 tons in 1895. The shipments generally go to San Francisco.

Apart from the ordinary yellow sulphur, which sometimes contains traces of selenium and tellurium, there occurs in Japan an orange-red variety, containing 0·17 per cent. Te, 0·06 Se, 0·01 As, traces of molybdenum and earthy matters (Divers and Shimidzu, Chem. News, 1883, No. 1256).

A considerable source of sulphur has recently been discovered on the volcanic island of Etrofu, about halfway between the northern extremity of Japan and Kamschatka. In 1900 already 10,000 tons sulphur were mined, and it is expected to reach 300 tons per month (Journ. Soc. Chem. Ind. 1901, p. 300).

A small island belonging to *New Zealand*, evidently the crater of a huge submerged volcano, which contains large deposits of sulphur, has been described by McIvor (Chem. News, 1887, lvi. p. 251). It will probably be very soon submerged as well. 1692 tons of sulphur were produced in that colony in 1900.

In the *United States of America* sulphur has been found in many places, particularly at Cove Creek, Millard County, South Utah; at Rabbit-Hole Springs, Humboldt County, Nevada; near Lake Charles, Louisiana; in Wyoming and other Rocky Mountain Territories; in Texas, California, and so forth. Very few of these occurrences are worked, either owing to the smallness of the stock or to the difficulties of carriage. The Rabbit-Hole mines have been worked off and on, but never at a considerable rate. For the purpose of working the best deposit, the Cove Creek mine, a Company (the Dickert and Myers Sulphur Company) was formed with a capital of $2,000,000, which acquired Dickert's patents, mentioned on p. 18; but it did not produce more than about 2000 tons of brimstone in 1886, and 2700 tons in 1887, so that it could not even supply all the needs of the Pacific coast, which amount to 4500 tons, and have to be made up from Sicily and Japan (details in the 'Mineral Resources of the United States,' Calendar years 1885, 1886, and 1887).

A very large deposit of sulphur has been discovered in the Grand Gulf Basin, near Lake Charles City, in the parish of Calcasieu, State of Louisiana. Two wells have been bored at different localities, which struck sulphur at a depth of about 450 feet. The first and thickest bed of sulphur is from 108 to 112 feet thick; it contains near the top 62 per cent., in the centre 90 per cent. of pure sulphur. One of the wells has been continued lower down, and proved the existence of several smaller beds of rich brimstone-ore, and several hundred feet of gypsum containing sulphur; in the other well no gypsum, but calcareous substance containing sulphur is found. The working presents a difficulty, as there are several hundred feet of quicksand on the top of the brimstone beds, which is to be overcome by the Frasch process (p. 18).

In Lower California, not far from the mouth of the Colorado River, a new bed of sulphur has been found. The crude sulphur contains 70 to 80 per cent. pure S (Fischer's Jahresb. 1897, p. 420).

According to the volumes of 'Mineral Industry,' the production, imports, and consumption of sulphur in the United States during the years 1896 to 1900 have been as follows (in long tons):—

Year.	Production. Tons.	Importation.				Consumption.
		Crude.	Flowers.	Refined.	Total.	
1891	1,071	116,971	206	10	117,187	118,208
1892	1,630	100,938	158	26	101,122	102,752
1893	1,200	107,601	241	41	107,885	109,020
1894	441	124,467	165	41	124,673	125,114
1895	1,650	125,950	581	229	128,410	128,410
1896	3,800	145,318	665	447	146,430	149,746
1897	1,690	138,846	319	148	139,313	140,849
1898	2,726	159,790	507	163	160,460	161,772
1899	1,565	140,841	336	184	141,361	142,449
1900	4,630	166,457	628	142	167,328	171,418

In *British Columbia*, on the Skeena River, a large deposit of sulphur has been found, and it was expected to supply the Puget Sound Country, and eventually the whole Pacific Coast, from this source (Journ. Soc. Chem. Ind. 1901, p. 1040).

In America sulphur is found also in many other places, as in the volcanic regions of Ecuador and Mexico, at Chillan in Chili, and elsewhere.

It has long been known that the crater of the Popocatepetl, in Mexico, contains large quantities of brimstone; and a railway has been projected in order to get at it. An annual production of 50,000 tons of brimstone was expected to begin with, and vitriol-works were to be erected all along the line (Fischer's Jahresb. 1884, p. 265). So far this project does not seem to have been carried out.

On the island of Saba, one of the Antilles, there is a bed of brimstone, yielding on an average 45 per cent. of sulphur, which was worked for some time, but had to be abandoned as not paying the expense (Dingl. Journ. 1886, cclix. p. 43).

In Chili brimstone is found at a height of from 12,000 to 13,000 feet above the sea. The mines, which were started in September, 1900, by an Iquique Company, are 54 miles from the nearest railway station. The product is said to be of very good quality; it is used in the provinces of Atacama and Tarapaca for the recovery of iodine and for making blasting-powder for the nitrate works. This seems to be the Taltal deposit mentioned in a Consular Report, quoted Journ. Soc. Chem. Ind. 1901, p. 1039. In 1901, the working was stopped as being at present unremunerative (Zsch. angew. Ch. 1901, p. 1243).

In Venezuela large beds of sulphur have been found, 20 or 30 miles distant from the coast, with which they are to be connected by a wire-rope line. The beds are to be worked by the Deutsch-Venezolanische Schwefelgruben A. G., at Cologne.

Sulphur Manufactured from other Materials.

Free sulphur is produced in large quantities in the manufacture of coal-gas, and is contained in the *spent oxide of iron.* We shall treat of this later on, as material for producing sulphur dioxide; in this place we mention it only as a source of obtaining free sulphur. This is sometimes done by extracting it with carbon disulphide; but this process does not generally seem to pay (comp. Journ. Soc. Chem. Ind. 1883, p. 491). Some of the processes described below are specially intended for this kind of material.

Broadberry (Gas World, 1895, xxiii. p. 643) extracts the sulphur from spent oxide of gas-works by means of benzol at a temperature of 70° or 80° C., employing a circulating-apparatus. 1 gallon of hot benzol yields on cooling 2·5 to 2·75 lbs. of solid sulphur, and retains 0·25 lb. in solution, which is obtained in distillation. From an experiment with 20 lbs., he calculates a profit of £1 6*s.* 3*d.* per ton of spent oxide.

The sulphur made from gas oxide is mostly of a dark colour, owing to the presence of a very small quantity of tarry substances, and this makes it very difficult to sell, so that it is nearly always burned without extracting it, as we shall see *infrà,* No. 5.

A certain quantity of sulphur is obtained by the *distillation of pyrites.* This, however, pays in very few places, except under special circumstances—for instance, at the works of J. D. Starck in Bohemia, which formerly supplied nearly all the fuming oil of vitriol, and where the distillation of pyrites is practised in order to obtain a material for the manufacture of sulphate of iron. Between 1863 and 1872, 2440 tons of sulphur were thus made. The distillation takes place in earthenware tubes 3 ft. 3 in. long, 5 in. high, and 5½ in. wide, quite open at the back, and in front narrowed to an opening of ¾ in. diameter; they are glazed with common salt; and three tiers of seven tubes each are placed in each furnace. For each tube there is a small receiver of sheet-iron half filled with water, and attached to the tapering end of the tube. The charge of pyrites is put into the open end; a slanting piece of sheet-iron is placed in front; and the opening is closed with sand or pyrites cinders, as shown in fig. 1.

Fig. 1.

Here only one-third of the sulphur contained in the pyrites is gained; but in Sweden half (?) of the sulphur is said to be obtained in a furnace built similar to a lime-kiln, and continued at the top in a wooden chimney serving as a condensing-space. The kiln, having been first made red-hot, is charged with pyrites, of which one portion is burned whilst the other portion volatilizes and is condensed at the top. The work is carried on continuously, fresh pyrites being from time to time introduced through an opening near the top, and the cinders being removed at the bottom.

P. W. Hofmann (Dingl. Journ. ccxx. p. 232) proposed to utilize the sulphur of the pyrites smalls. If sulphur dioxide is conducted over red-hot calcium sulphide (from alkali-waste), it is at first completely absorbed; afterwards sulphur distils over, and the calcium sulphide is transformed into sulphate. The latter, by conducting ordinary coal-gas over it in a red-hot state, or by mixing it with coal and igniting, is reconverted into sulphide, which can be used over again. Hofmann proposed to burn the pyrites smalls at the mines, to obtain their sulphur by means of calcium sulphide in a state fit for sale, to treat the cinders by a process to be described in the 13th Chapter for zinc chloride and sodium sulphate, and to work the residue for pig-iron in a blast-furnace. This proposal has not found any application in practice, and is not likely to do so, since the burning of pyrites dust by the shelf-furnace is quite as advantageous for acid-making as that of lump ore.

Gerlach (German patent 229, 1877) proposed to obtain sulphur from sulphur-ores, and especially from the spent oxides of gas-works, by heating them in iron or fireclay retorts whilst at the same time superheated steam is passed through. The sulphur is said to distil very rapidly. A description of this process, with diagrams, is found in Wagner's Jahresb. 1879, p. 268. It was tried in Upper Silesia with sulphur marl, but did not answer (Fischer's Jahresb. 1882, p. 234).

O. C. D. Ross patented a process in every way similar to Gerlach's (E. P. No. 713, 1879). Other processes of the same kind are described in the 'Scientific American,' xxxix. p. 276, and in the 'Chemiker-Zeitung,' 1879, p. 241, by Dubois (E. P. No. 13,108 of 1885 and No. 7129 of 1886; G. P. 41,718: the last patent describes a revolving retort).

According to a French patent of the Société de St. Gobain (No. 107,820, 28th April, 1875), on the top shelf of an ordinary shelf-burner for pyrites smalls (see Chapter IV.) a fireclay retort is to be placed, in which the pyrites is first deprived, by distillation, of a portion of its sulphur, which is collected in the well-known condensing-chambers as flowers of sulphur. After some time the partially desulphurized pyrites is let down to the next lower shelf, and so on to others lower down. Here the remainder of the sulphur burns, and the gas goes into acid-chambers, whilst its heat causes the distillation of further portions of pyrites in the retort. This process does not answer: the flowers of sulphur obtained is very acid; and both the burner and the chambers work very badly. A similar process has been again patented by Labois (E. P. No. 9761 of 1884).

Buisine (Germ. pat. 73222) heats half-roasted pyrites with sulphuric acid, to recover sulphur, ferrous sulphate being obtained as by-product. According to pat. 79706, the pyrites is to be distilled in closed vessels at 700° C. and the residue treated as above with sulphuric acid. The residue, consisting of sulphur and ferrous and cupric sulphate, can be applied as it is to vines for certain diseases; or else it is extracted with water, the residue is worked for sulphur, and the solution, by treating it with metallic iron, yields metallic copper and ferrous sulphate.

Holloway's process (E. P. No. 500 and 1131, 1878) at one time excited much attention. He blows heated air through melted iron sulphide, thus decomposing it into a cupreous matt and a slag, together with free sulphur, which distils off and can be collected. The principal aim of this process was the concentration of poor copper-ores in countries where fuel is expensive. It has been described by the inventor in a paper read before the Society of Arts, which has been published together with the discussion following the reading of the paper. Bode (Dingl. Journ. ccxxxii. p. 433) has criticised it. Dr. Angus Smith (Alkali Reports, 1877–78, p. 47) expected important results from this process, which is decidedly very interesting; but it has found no practical application.

Stickney (Eng. & Min. Journ. lxv. p. 674) heats pyrites to red heat by means of producer-gas. There is an escape of H_2S and SO_2, which are converted into free sulphur by means of a spray of salt solution (comp. Schaffner's and Helbig's process, vol. ii. 2nd edition of this work, p. 857); the reaction is to be promoted by electric sparks.

Fröhling, Fleming, and Whitlock (E. P. 10,295, 1900) intend to obtain practically all the sulphur from FeS_2 by heating the ore in a retort in a stream of carbon dioxide or nitrogen with the addition of a small regulated quantity of oxygen, by which only the iron is burnt to Fe_2O_3, the sulphur being set free.

It has often been proposed to prepare sulphur by *passing gases containing sulphur dioxide through red-hot coal.* A special apparatus for this purpose has been proposed by Haenisch and Schroeder (E. P. 6404, 1885). They pass the first gases through fire-clay cylinders filled with coke and heated from the outside by producer-gas; the products of combustion travel through another cylinder, filled with open brick-work and heated by the waste fire-gases of the first operation; here the undecomposed SO_2, the carbon monoxide, carbon disulphide, and carbon oxysulphide act upon one another, so that, if the current has been properly regulated, ultimately only CO_2 and S are formed. Or else the SO_2 is at once treated with CO, according to the equation

$$SO_2 + 2CO = 2CO_2 + S.$$

This process has been tried on a large scale at Oberhausen (comp. Chem. Zeit. 1886, p. 1039, abstracted in J. Soc. Chem. Ind. 1886, p. 534), but evidently not successfully.

J. and F. Weeren obtain the SO_2 for this purpose by calcining sulphates with silica (G. P. 38,041). They describe a special apparatus for this reduction and the reduction of the SO_2 by incandescent coke to S.

Heinrici (Zsch. angew. Ch. 1898, p. 525) employs this reaction for the purpose of utilizing the acid tar formed in the purification of mineral oils. By heating this SO_2 is evolved, which is reduced to free S by red-hot coke.

Sulphuretted hydrogen has been very frequently proposed as a material for the production of free sulphur, which has become an economical possibility through the Claus process. We cannot describe this industry in this place; it is fully dealt with in vol. ii. of the 2nd edition of this work, page 891 *et seq.*, and we subjoin only a brief notice of some improvements proposed since 1896.

Carulla (J. Soc. Chem. Ind. 1897, p. 980) prefers burning H_2S in an ordinary pyrites-kiln, in lieu of the Claus kiln, as the yield is much larger.

Baranoff and others patent (E. P. 7269, 1898) the production of S from H_2S, obtained by the reduction of native sulphates and treatment by CO_2. This H_2S is passed over red-hot sulphates, which are thereby reduced and yield free S and SO_2.

Palaschkowski (Russ. pat. 5464 and 5477, 1901; Chem. Zg. 1902, p. 15) describes the following modifications of the process of Baranoff and Hildt for obtaining S and SO_2 from sulphates. Instead of simply mixing the sulphates with coke, he moulds them into briquettes by means of coal-tar, &c., which shortens the time of reduction. The sulphide is decomposed by CO_2 at a pressure of 2 or 3 atmospheres. The H_2S is best not passed at once through red-hot sulphates, but first through a solution of the sulphides, which forms $Ca(SH)_2$ and NaHS. The former is converted by means of Na_2SO_4 into NaHS, which with CO_2 gives H_2S and $NaHCO_3$. Only this H_2S is employed for being oxidized by sulphates to S and SO_2.

Davidson and the United Alkali Co. (E. P. 17476, 1897, and 7088, 1898) describe improvements in the subliming of sulphur.

Albright and Hood (E. P. 11988, 1894) purify sulphur by heating it for some time just below its boiling-point.

The world's production of sulphur is stated as follows in Min. Ind. ix. p. 611, from official sources, in metric tons :—

Country.	1895.	1896.	1897.	1898.	1899.
Austria	830	643	530	496	555
France	4,213	9,720	10,723	9,818	11,744
Hungary	102	138	112	93	116
Germany	2,061	2,263	2.317	1,954	1,663
Greece	1,480	1,540	358	135	1,150
Italy	370,766	426,353	496,658	502,351	563,697
Japan	15,557	12,540	12,013	10,339	10,241
Russia	190	437	574	?	?
Spain	2,231	1,800	3,500	3,100	1,100
Sweden	nil.	77	nil.	50	nil.
United States	1,676	3,861	1,717	2,770	1,590

The sulphur produced as a by-product of the Leblanc process by the Chance-Claus process in Great Britain is not included. This is estimated for 1898 at 31,000 tons.

Technical Analysis of Sulphur.

The first quality of Sicilian sulphur (prima Lercara or prima Licata) is of a fine amber colour, in large shining pieces, and does not contain more than 1 per cent. ash. The second quality (seconda vantaggiata) is still fine yellow, but not so shining, with ash up to 2 per cent.; the third (terza vantaggiata), which is that generally used for sulphuric-acid making, contains up to 5 per cent. ash and is coloured brown, partly by bituminous substances, partly by amorphous sulphur. "Zolfo ventilato" (manufactured by Walter and Trewhella at Naples, Fischer's Jahresb. 1901, p. 406) is sulphur, finely ground, raised by a chain of buckets and sifted by the action of a current of cooled furnace-gases (which produce less danger of fire than air would do, as they contain less oxygen).

The ordinary *technical assay* of brimstone is performed by burning a weighed quantity, say 10 grams, in a small porcelain capsule, and estimating the quantity of ash left behind. It is, however, advisable to estimate also the moisture, for which purpose, in order to prevent any evaporation during grinding, an average sample of the unground or merely roughly-crushed material, weighing 100 grams, is dried at 100° C. for some hours in an oven or water-bath.

Bituminous substances are most easily recognized by the colour of the sulphur; they occur chiefly in sulphur made from spent oxide of gas-works, which is sometimes coloured quite black.

Arsenic sometimes occurs in brimstone, more especially in that recovered from alkali-works, always in the shape of arsenious sulphide. On extracting the brimstone with disulphide of carbon, the As_2S_3 remains behind and can be estimated. Schaeppi (Chem. Ind. 1881, p. 409) prefers extracting the As_2S_3 with dilute ammonia (as described by the German Pharmacopœia) at 70° or 80° C. In the solution the sulphur can be precipitated with silver nitrate as Ag_2S, which is filtered, washed, dissolved in hot nitric acid, and estimated as chloride; 6 molecules of AgCl correspond to 1 of As_2S_3. It is, however, more expeditious to work volumetrically. The ammoniacal solution of arsenious sulphide is exactly neutralized with pure nitric acid, strongly diluted and titrated with decinormal silver nitrate, till a drop of the solution, on addition of neutral potassium chromate, produces a brown colour. When employing 10 grams of sulphur for extraction with ammonia, each c.c. of decinormal silver solution indicates 0·041 per cent. As_2S_3. Sometimes arsenic occurs in recovered sulphur in the shape of ferric or calcium arsenite, which cannot be found by the above process, but only by extracting the sulphur with carbon disulphide and digesting the residue with aqua regia.

A qualitative reaction for arsenic consists in agitating 1 gram sulphur with 15 drops liquor ammonia and 2 c.c. water for half an hour, filtering, adding to the filtrate 30 drops of hydrochloric acid and 15 drops solution of oxalic acid, placing a bright piece of brass in the solution and heating to 60°–100° ; in the presence of arsenic the brass is stained grey or black (Hager, Pharm. Centr. 1884, pp. 263 & 443).

Selenium is discovered by deflagrating the sulphur with nitrate of potash, dissolving in hydrochloric acid, and treating with SO_2, which precipitates the selenium as a red powder.

Reed (Chem. Zeit. 1897, Rep. p. 252) describes the American test for selenium. Boil 0·5 gram sulphur with a solution of 0·5 gram potassium cyanide in 5 c.c. water, filter and acidify the filtrate with HCl; a red colour, appearing within an hour, shows selenium. Or else boil 1 gram sulphur with a solution of 2 grams potassium cyanide for an hour, add another 0·5 gram KCy and boil for another half-hour. Of course any iron present will react with the sulphocyanide formed.

Macagno (Chem. News, xliii. p. 192) proposed the *direct estimation of sulphur* by means of its solubility in carbon disulphide *. Pfeiffer (Zsch. anorg. Ch. xv. p. 194, and Lunge, Chem. techn. Untersuchungs methoden, i. p. 240) has re-investigated this matter and given the following prescriptions for this method:—Shake a weighed sample of powdered sulphur with exactly four times the quantity of pure carbon disulphide, filter, reduce the temperature to 15° C., and ascertain the specific gravity of the solution. The following table (abridged from the original) shows the number of parts of sulphur dissolved by 100 parts by weight of CS_2 at 15° C. for various specific gravities found:—

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* F. B. Carpenter (Journ. Soc. Chem. Ind. 1902, p. 832) points out that crude sulphur sometimes contains a large quantity of gypsum which interferes with the carbon-disulphide treatment. In such cases the calcium sulphate must be previously removed by boiling with hydrochloric acid.

Specific gravity.	Sulphur dissolved.	Specific gravity.	Sulphur dissolved.	Specific gravity.	Sulphur dissolved.
1·2708	0	1·3087	8·5	1·3426	17·0
1·2731	0·5	1·3108	9·0	1·3445	17·5
1·2754	1·0	1·3129	9·5	1·3463	18·0
1·2779	1·5	1·3150	10·0	1·3481	18·5
1·2800	2·0	1·3170	10·5	1·3500	19·0
1·2833	2·5	1·3190	11·0	1·3517	19·5
1·2847	3·0	1·3211	11·5	1·3536	20·0
1·2870	3·5	1·3231	12·0	1·3553	20·5
1·2894	4·0	1·3251	12·5	1·3571	21·0
1·2916	4·5	1·3271	13·0	1·3587	21·5
1·2938	5·0	1·3291	13·5	1·3605	22·0
1·2960	5·5	1·3311	14·0	1·3622	22·5
1·2982	6·0	1·3330	14·5	1·3640	23·0
1·3003	6·5	1·3350	15·0	1·3657	23·5
1·3024	7·0	1·3369	15·5	1·3674	24·0
1·3045	7·5	1·3388	16·0	1·3692	24·5
1·3066	8·0	1·3408	16·5	1·3709	25·0

The same subject is again treated by P. Fuchs (Zsch. angew. Ch. 1898, p. 1189). His figures are slightly different from those of Pfeiffer; but the latter's results (which were obtained in my own laboratory) seem to me the most accurate obtainable.

For the purpose of preventing the grape-disease (the *Oïdium*) the *degree of fineness* of ground sulphur is very important. In France this is ascertained by Chancel's *sulphurimeter*, shown in fig. 2 on a scale of 1 : 2. This is a glass tube sealed at the bottom and closed at the top by a ground-in glass stopper. It is 23 cm. long and 15 mm. wide, and divided into 100 degrees of ¼ c.c. each, beginning from the bottom; the 100 degrees occupy a space of 100 mm.

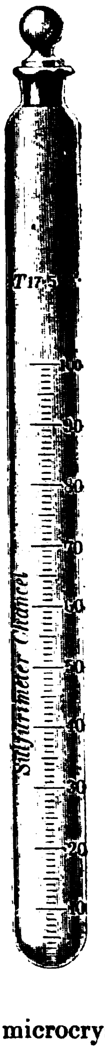
If ground sulphur is shaken up with anhydrous ether it forms, after settling down, a layer, the height of which corresponds to the fineness of the powder. The sulphur to be tested is passed through a sieve with meshes 1 mm. wide; 5 grams of it are put in the tube, together with ether of 17°·5 C., or very nearly that temperature, filling half the tube. The tube is well shaken to break up all small lumps, more ether is poured in up to 1 cm. above the degree 100, the tube is again shaken and placed in a vertical position. When the layer of sulphur ceases to subside, its height is read off and stated as "degrees Chancel."

Ordinary ground and sifted sulphur shows 50° to 55° Chancel, finer grades 70° to 75°. The finest grade is obtained not by sieving, but by fanning—this "zolfo ventilato" shows 90° to 95° Chancel (Walter, Chem. Zeit. 1901, p. 459; *suprà*, p. 31). For use in vineyards the sulphur ought to show at least 60° Chancel; some go as far as 75° Chancel.

Analysis of refined sulphur.—Sulphur in blocks or rods is almost always practically pure; it may be tested for ashes, arsenic, and selenium as above.

Flowers of sulphur is never quite pure unless specially washed; it always contains some acid. Ianda (Fischer's Jahresb. 1898, p. 421) found up to 0·283 per cent. ashes; the average of 30 samples was 0·063 per cent. He also tests the solubility in boiling solution of caustic soda of spec. grav. 1·2. This varied from 88 per cent. (in one case 68 per cent.) to 99·99 per cent., average 98·04 per cent.

Fig. 2.



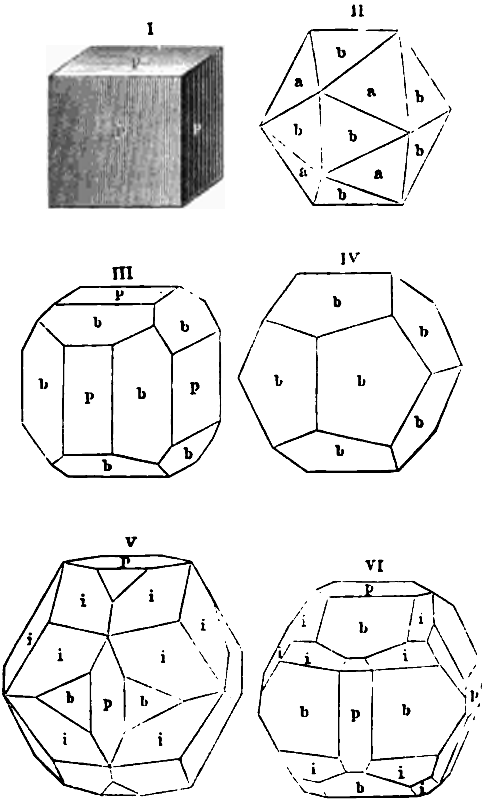
2. PYRITES.

What is called *pyrites* or *iron-pyrites*, in a technical sense, is hardly ever pure iron disulphide, FeS_2, but either a mixture of this with gangue, or more frequently at the same time with other sulphuretted ores, as shown by numerous analyses. The iron disulphide may be present either as iron-pyrites proper or as marcasite. The iron-pyrites proper crystallizes in the regular system, with parallel hemihedry, proved even on the faces of the cube by striation (fig. 3).

Besides the cube (I), the octahedron, *a* (II), is frequently found, often modified by the pyritohedron, *b* (III), and, if both are equally developed, forming the icosahedron (II). The combined forms IV, V, VI, as well as twin crystals, frequently occur. The crystals are often well developed; but in the pyrites used on the large scale they are mostly quite indistinct. The colour of pure pyrites is greyish yellow, and easily distinguished from that of copper-pyrites. The microcrystalline pyrites of trade often shows other colours, even a slate-grey; the powder is brownish black. Its cleavage parallel to the faces of the cube is not very pronounced; the fracture is conchoidal or irregular. Hardness 6 to 6½, specific gravity 4·83 to 5·2. Pure FeS_2 contains 46·67 per cent. of iron and 53·33 per cent. of sulphur.

According to Mène, the pyrites from volcanic formations contains no water, but that from sedimentary strata both water and clay. Among the first he classes the yellow octahedral pyrites, which is stable in the air; among the latter the grey cubical pyrites, which is easily transformed into ferric sulphate (Compt. rend. 29th April, 1867).

Fig. 3.



Marcasite crystallizes in the rhombic system, in rhombical prisms $m = 106^\circ 2'$ with longitudinal faces $l = 100^\circ$ and r, and the end face p inclined to r at an angle of 158° 20′. They frequently occur in twin crystals, partially united along one of the faces *m*, also in triplets and quadruplets, &c. (fig. 4), in fibrous, bulbous, &c. varieties; cleavage indistinct; hardness 6 to 6·5; specific gravity 4·65 to 4·88; colour grey to yellow or greenish yellow, lighter than iron-pyrites proper; powder greenish dark grey. Marcasite is most frequently found in bituminous slate and coal, and decays even more quickly than pyrites, with the formation of ferrous sulphate and basic ferric sulphate.

Fig. 4.

Detailed investigations on the different behaviour of pyrites and marcasite have been published by A. P. Brown (Chem. News, 1895, lxxi. p. 139, and following numbers) and by Stokes (Bulletin U.S. Geol. Surv. No. 186, 1901).

In the ores of commerce there is often present, mixed with FeS_2, *magnetic pyrites* (*pyrrhotite*) of the formula Fe_7S_8, with 60·5 iron and 39·5 sulphur; colour between brass-yellow and copper-red; hardness 3·5 to 4·5; specific gravity 4·4 to 4·7. Pyrrhotite occurs by itself in large quantities, which have been scarcely utilized up to the present.

The *copper-pyrites* so often mixed with iron-pyrites is distinguished from it by its colour, yellow as brass, sometimes as gold; this colour modifies that of the iron-pyrites according to the degree of admixture. It crystallizes in the tetragonal system, but in the ores which concern us always occurs in a microcrystalline form. Its hardness is 3·5 to 4·0, specific gravity 4·1 to 4·3. Pure copper-pyrites of the formula $FeCuS_2$ should contain 30·53 per cent. iron, 34·58 per cent. copper, and 34·88 per cent. sulphur; but the ores serving for the manufacture of sulphuric acid rarely contain beyond 4 per cent. of copper.

The first application of pyrites for sulphuric-acid making is generally ascribed to a Mr. Hill, of Deptford, who in 1818 took out a patent for it *. In France, Clément-Desormes seems to have made the first proposals and experiments in that way. His trials did not, however, succeed, because he believed it necessary to increase the combustibility of pyrites by an addition of coal. This is both unnecessary, with properly constructed kilns, and very injurious

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* Sorol attributes this honour to his countryman, d'Artigues, in 1793.

to the process, from the carbonic acid getting into the chambers. A great difficulty was experienced in lighting the kilns. So long as it was attempted to do this from below, like an ordinary fire, the thing would not work. According to communications from Mr. Todd (Government Inspector of Alkali Works), a workman of his father's in Cornwall, in 1830, accidentally discovered the way of lighting the kilns from the top, such as is practised to this day. Generally, however, the principal merit of introducing pyrites is ascribed to Messrs. Perret and Son, of Chessy, who were led to it by the necessity of desulphurizing their cupreous pyrites previously to getting the copper, and of condensing the gas evolved. There was no question then of supplanting the Sicilian sulphur generally. Perret and Son, with the greatest care, searched into all the conditions necessary for a proper combustion of the ore; and to them the honour is due of having overcome all the difficulties opposed to the solution of this problem, and of having rendered the process technically useful. Already in 1833 they had burnt iron-pyrites successfully; and in a patent dated November 20th, 1835, they described their process, to which their partner, Olivier, is said to have given the first impulse. In 1837, Messrs. Wehrle and Braun, in Bohemia, used pyrites for generating sulphurous acid (Otto, 'Lehrbuch der Chemie,' 4th ed. iii. 1, p. 545); but, according to Bauer (*l. c.* p. 6), I. Brem had introduced this process into Austria (at Lukawetz) already in 1833—that is, at the same time as Perret.

These trials at making sulphuric acid from pyrites possessed, however, only local interest; and probably for a long time no general attempt to do away with Sicilian brimstone would have been made, but for the Neapolitan Government, in 1838, being induced to grant a monopoly for the exportation of Sicilian sulphur to the Marseilles firm of Taix and Co. This firm at once raised the price of brimstone from £5 to £14 per ton, and thus would have given a fatal blow to the manufacture of artificial soda-ash, just then beginning to take a firm hold, if no other source of sulphur had been known, and if such an unnatural measure could have been carried out at all. But the attempt came too late—just after Perret and Son had proved that the pyrites occurring in most industrial countries could be used for vitriol-making without any difficulty. The result was to be foreseen. Once the discovery of a new source of sulphur had become a matter of necessity, there were, within twelve months from the rise in the price of brimstone, fifteen patents taken out in England for burning pyrites for the purpose of making sulphurous acid, and even a larger number for making sulphur from pyrites, gypsum, &c.

According to Muspratt's 'Chemistry' (vol. ii. p. 1023), Dr. Thomas Thomson was the first in England to point to pyrites in this crisis; but most probably many others at the same time turned to it. So much is proved—that Thomas Farmer, of London, was the first in England who employed pyrites on a large scale (in 1839) for the manufacture of sulphuric acid (Hofmann, 'Report by the Juries, International Exhibition, 1862, Class II. Section A,' p. 12).

Mr. E. K. Muspratt states that his father, in 1839 and 1840, used large quantities of Wicklow and Welsh pyrites at Liverpool and Newton, the cupreous cinders being sent to the Sutton Copper Company at St. Helens.

In Germany the Oker works, at the Rammelsberg, near Goslar, seem to have been the first who calcined the local ore in such a way as to convert the sulphurous acid given off into sulphuric acid in acid-chambers; and other smelting-works, such as those at Freiberg, followed their example. In these cases the reasons were, not only that at a comparatively small expense sulphuric acid could be obtained as a by-product from the sulphurous acid otherwise lost, but also that the acid fumes destroyed the vegetation of a large district round the works, and that means had to be taken for preventing this, apart from any consideration of profit.

The Sicilian brimstone monopoly certainly did not last long; diplomatic pressure on the part of England soon led to its abolition; and with the lowering of the price of brimstone most works at first returned to its employment. But the ice was now broken; the conviction had been gained that it was possible to make acid without Sicilian brimstone; the owners of pyrites-mines took pains to advance the use of pyrites by low prices; and thus, in the course of the next twenty years, brimstone was gradually, but steadily, driven from its place in sulphuric-acid making, in proportion as, on the one hand, it became dearer from the causes above mentioned (disease of the vines &c.), and as more pyrites-mines were opened out. In 1852 brimstone was no longer used in Lancashire, but on the Tyne 7580 tons of it were still burned.

The decisive point in favour of the use of pyrites was this, that continually increasing quantities of *cupreous pyrites* came into the market, from Spain especially (first in 1859), but also from other countries. These had at any rate to be burnt and their sulphur expelled before they could be worked for copper. Already with Perret and Son this had been the stimulus for their efforts; but this has been done on a much more colossal scale in consequence of the opening out of the cupreous-pyrites mines in the south of Spain, in Portugal, and in Norway. In England iron-pyrites is now all but out of the field, and has been supplanted by cupreous pyrites. This has been the case to a less extent in France and Germany, because they possess mines of rich iron-pyrites, which in England are not numerous; but even in those countries more cupreous pyrites is now used. In 1867 pyrites had almost entirely supplanted brimstone in France as a raw material for acid-making in the large industrial centres (‘Rapport du Jury International, Expos. Univ. de 1867,’ vol. vii. p. 19). In Germany this state was brought about somewhat later, but quite as completely. Only during the feverish years 1871 to 1873, when the price of pyrites had risen very high, a few factories in Hanover, in Hamburg, and Stettin temporarily returned to the use of brimstone (Hasenclever, *l. c.* p. 155); but with lower prices of pyrites this was given up again. Spanish pyrites began to be used in Germany in 1877.

Thus, starting from the use of iron-pyrites, that of cupreous pyrites has followed; and to this was added the employment of other sulphurous ores and of the intermediate products of smelting —for instance, copper-regulus (“coarse metal”) at Mansfield and Swansea. The first chambers working with SO_2 from the metallurgical treatment of copper and lead ores were started at Oker in 1859, at Freiberg in 1861. The Freiberg works employ for this purpose even poor lead-matts with about 22 per cent. of sulphur, which formerly was thought impossible (Bode, ‘Beiträge zur Theorie und Praxis der Schwefelsäurefabrikation,’ 1872, p. 1). We shall further on describe the application of other sulphur-ores apart from pyrites proper.

The *principal sources of pyrites* will now be mentioned without separating the cupreous from the non-cupreous, because no strict limit can be drawn. Some kinds of pyrites contain so little copper (below 1 per cent.) that it cannot be utilized; and these go with the totally non-cupreous ores.

Great Britain possesses several deposits of pyrites, but none of very great importance. In Cornwall and Devonshire pyrites of the following composition is found:—

	Pattinson.		Clapham (8 analyses).
Sulphur	27·00		24·013–34·880
Iron..................	22·69		27·076–60·676
Copper	2·00		0·400– 4·600
Lead	trace		0· – 7·446
Zinc..................	1·23		0· – 9·086
Lime	0·22	Gypsum	0· – 0·596
Carbonate of Lime	......		0· – 3·579
Magnesia...........	0·12		
Arsenic	0·32		0· – 1·160
Insoluble (silica)...	45·60		2·000–38·676
Oxygen as Fe_2O_3...	0·13		
Moisture	0·64		
	99·95		

Cleveland pyrites (from the north of Yorkshire) is only used in a local factory; in 1874, 500 tons of it were obtained. Composition (according to Pattinson's analysis):—

Iron disulphide........................	52·12
(corresponding to 27·18 sulphur).	
Iron protoxide	11·92
Alumina	8·10
Lime....................................	0·27
Magnesia	1·00
Carbonic acid	2·40
Insoluble in acid	11·12
Water	12·86
	99·79

In *Ireland* there are large beds of pyrites, especially in the county of Wicklow; and up to about 1862 this Irish ore supplied a very large portion of the pyrites used in England. In 1860 still 40,000 tons of it were imported into the Tyne River; but in 1863 the importation had fallen to 4000 tons, and has long since ceased entirely. The same has been the case in Lancashire; and only a few works in Ireland itself burn this kind of pyrites. It is found in the county of Wicklow in beds from 6 to 50 feet in thickness, which overlie siliceous clay-slate. The beds go down to depths of 80 to 100 fathoms. The bulk of the ore contains only 30 to 35 per cent. of sulphur. A small quantity only of richer ore (analyses *a, b, c*) has been found in the valley of Ovoca. The Irish ore is too hard and slaty and does not burn well; it requires a great heat, and consequently deep kilns. It nearly always contains copper, but rarely sufficient to pay for extracting it, from which standpoint the following analyses must be judged:—

	Pattinson.	Clapham.			
	a.	*b.*	*c.*	*d.*	*e.*
Sulphur............	44·20	40·410	42·128	37·975	34·676
Iron	40·52	32·222	35·000	34·650	42·400
Copper	0·90	4·133	2·400	2·400	1·333
Lead	1·50	2·963	1·600	1·080	1·593
Zinc	3·51	...	...	...	...
Arsenic	0·33	...	0·602	0·400	0·183
Lime	0·24	...	...	...	...
Insoluble	8·80	17·676	18·676	22·500	20·000
Moisture	0·09	...	...	...	...
Oxygen as Fe_2O_3..	0·25	...	...	...	...
	100·34	97·404	100·406	99·005	100·185

In *Wales* (in the Cae Coch Mine) pyrites is found entirely free from arsenic, according to Drinkwater (Journ. Soc. Chem. Ind. 1885, p. 533). It contains 48·3 per cent. of sulphur, and is used for manufacturing very pure oil of vitriol.

A certain quantity of pyrites is picked from coals, and is known as *coal-brasses*. If quite free from coal, they are very rich—according to R. D. Thompson (in Richardson & Watts's 'Chemical Technology,' vol. i. pt. iii. p. 15), 53·55 sulphur, 45·07 iron, 0·70 manganese, 0·80 silica; but practically they cannot be obtained in this state, and the carbonaceous matter adhering to them causes very much trouble in the vitriol chambers. Their principal use in acid-making is for lighting the burners, or for getting up their heat if it has gone down. Mr. G. E. Davis informs me that coal-brasses with 44 per cent. S and some carbon can be burnt in ordinary pyrites-kilns, and, if proper arrangements are made, yield perfectly clear acid from the Glover tower. Apart from this they are worked up by weathering for copperas and Venetian red, and this is probably the way in which most of the quantity obtained in England (10,000 tons in 1874) is consumed.

The total production of pyrites in the United Kingdom was 25,401 tons in 1882, 27,829 tons in 1886; in 1887, 22,079 tons; in 1888, 23,507 tons; in 1889, 17,719 tons; in 1890, 16,018 tons; 1895, 9193 tons; 1896, 10,177 tons; 1897, 10,752 tons; 1898, 12,302 tons; 1899, 12,426 tons; 1900, 12,484 tons.

The *importations of foreign pyrites* into Great Britain during the years 1862 to 1887 are quoted in our second edition, vol. i. p. 32. Here we shall quote (from the volumes of 'Mineral Industry') the importations of pyrites (iron and cupreous) into Great Britain since the year 1888. (The tons are metrical tons at 1000 kils. = 0·9842 English ton.)

Year.	Pyrites imported. Tons.
1888	629,056
1889	654,872
1890	667,625
1891	662,297
1892	614,238
1893	622,634
1894	625,968
1895	591,782
1896	598,480
1897	633,009
1898	665,544
1899	712,393
1900	752,605

The most important *German* pyrites-bed is that of *Meggen* in the Siegen district, in Westphalia, 3 miles from the Altenhunden station on the Ruhr-Sieg railway. This bed occurs along with heavy spar in the so-called "Kramenzel;" it is known for a length of 2000 fathoms, and its thickness changes from ¾ to 3 fathoms (Wagner's 'Jahresbericht,' 1865, p. 221). The same authority states it to be "grey iron-pyrites," quite uncrystalline, free from arsenic [?]. The mass of ore above the bottom of the valley is estimated at 4¼ million tons; how far the ore descends below the bottom of the valley is as yet unknown.

The ore has not an attractive outward appearance; its colour is slate-grey; but it burns very well in the kilns, and it would be even more valuable if the zinc contained in it did not prevent its burning completely. Older analyses of it are given in our 2nd edition, vol. i. p. 35. Here I quote the most recent analyses made at the Rhenania Chemical works, as furnished to me by Dr. R. Hasenclever in 1902:—

	a.	*b.*	Average.
Gangue	12·02	12·96	12·0
Sulphur	41·94	43·42	40·0–43·0
Iron	34·92	35·56	35·0
Zinc	7·56	5·81	7·0
Lead	0·38	not estim.	0·3–0·5
Lime	0·50	,,	0·1–0·5
Arsenic	trace	0·05	trace–0·05
	97·32	97·80	

The average represents 12 per cent. gangue, 75 per cent. iron-pyrites (FeS_2), 10·5 per cent. zinc-blende (ZnS), together 97·5.

Jurisch (Schwefelsäure-fabrikation, p. 14 *et seq.*) quotes a number of analyses of Westphalian pyrites, by F. Quincke, for the year 1892. In these the sulphur varied from 41 to 46·75 per cent., iron from 29·55 to 36·16 per cent., zinc from 8·2 to 19·41 per cent. (I exclude two samples containing 27·58 and 42·05 per cent. zinc, which are more correctly classed as blende than as pyrites), lead from 0·3 to 1·7 per cent., arsenic from 0·1 to 0·2 per cent., besides silica, alumina, lime, magnesia, manganese, alkalies, and small quantities of other substances.

The same source quotes analyses of pyrites from Bensberg (46·86 per cent. S), Aachen (46·0 per cent.), Rammelsberg (44·65 to 48·4 per cent.), Freiberg (52·20 per cent.).

The following is a complete analysis by Fresenius of ore from the Philippine pit belonging to the Sicilia Mining Company at Meggen, made in 1898:—

Iron	34·89
Zinc	8·38
Manganese	0·155
Cobalt and Nickel	0·024
Lead	0·298
Alumina	trace
Lime	1·41
Magnesia	0·75
Sulphur	44·55
Arsenic	0·07
Carbon dioxide	1·90
Phosphorus peroxide	trace
Gangue	5·83
Oxygen as sulphate, thiosulphate, &c., and traces of other substances	1·743
	100,000

There are smaller beds of pyrites in several other places in Germany, such as those near Goslar, near Schwelm in Westphalia, near Merzdorf in Silesia, &c. Their production is only small compared with that of the Meggen pyrites. The pyrites of the Rammelsberg in the Harz, according to Mène, contains 48·4 per cent. of sulphur (probably only picked lumps). The cupreous pyrites of the same place is stated by Hilgenfeld to contain:—

Copper	12·22
Lead	2·43
Iron	39·10
Zinc, Manganese, Cobalt, Nickel	1·23
Arsenic	0·18
Antimony	0·16
Sulphur	44·65
Selenium, Thallium, Indium, Bismuth	traces
	99·97

The bed of *Schwelm* in Westphalia, in the Devonian formation, has a thickness of from 10 to 33 feet, over a surface of nearly 150 acres, and is covered by rich iron-ore; the pyrites itself consists of two-thirds powder mixed with well-crystallized pieces.

The ore contains about 40 per cent. sulphur, and more or less clay, which is removed by washing; after this it is sold to the vitriol-makers, who like it on account of its freedom from arsenic (Dingl. Journ. ccxxviii. p. 283); Hjelt, however, found more arsenic in it than in Meggen pyrites.

On the island of Wollin a pyrites-bed is found in a bed of marl belonging to the chalk formation.

A great drawback to the German ores is their proportion of zinc, which retains a considerable quantity of sulphur in the state of sulphate. In Silesia 14 per cent. of zinc is allowed as a maximum; upwards of this for each per cent. of zinc the same quantity of sulphur is deducted from the invoice (Kosmann, in Fischer's Jahresb. 1886, p. 268).

The production of German pyrites during the years 1853 to 1886 is quoted in the second edition of this work, vol. i. p. 38; that between 1891 and 1897 by Hasenclever, Chem. Ind. 1899, p. 25.

The maximum production in 1874 was 143,476 tons; the average of the last years is about 130,000 tons. The production was 133,302 tons in 1897, 136,849 tons in 1898, 144,602 tons in 1899. Hasenclever estimates that about 65,000 tons was consumed in the manufacture of wood pulp. The importation of foreign (chiefly Spanish) pyrites into Germany increased from 238,643 tons in 1891 to 357,017 tons in 1897, all of this for sulphuric acid. In 1898 it was 376,817 tons, in 1899 437,732 tons, in 1900 457,679 tons.

The exportation is small: in 1898 19,219 tons, in 1899 16,985 tons, in 1900 24,936 tons.

Austria-Hungary possesses large beds of pyrites at Schemnitz and Schmölnitz in Hungary, in Styria, and Tirol. The pyrites from Schemnitz contains on an average 47 to 48 per cent. S, 39 to 40 per cent. Fe, 0·58 per cent. Cu, 1·5 to 2 per cent. Zn, besides lead, silver (81 grams per ton), and gold (2·2 grams per ton). Schmölnitz ore contains 44 to 48 per cent. S, 0·4 to 0·6 per cent. Cu, 2 to 3 per cent. Zn. Jurisch (from whose 'Schwefelsäurefabrikation,' p. 18, the above is taken) quotes an analysis of Schmölnitz pyrites with 48·89 per cent. S, 0·32 per cent. Cu, 0·14 per cent. As; 70,000 or 80,000 tons of this pyrites are obtained per annum.

In *Tirol* pyrites is found testing 40·5 to 41·3 per cent. S.

In *Styria* (Riedl, Zeitschr. f. d. chem. Grossgewerbe, ii. p. 567), in the Saun valley, a number of beds of very pure but easily decomposable pyrites occur in the clay porphyry, with a percentage of 48 to 52 of sulphur. It is used in the chemical works at Hrastnigg and in Bohemia. The production is about 3000 tons per annum (Fischer, Jahresb. 1886, p. 255).

In *Switzerland*, in the Canton of Wallis, a pyrites is obtained which does not seem to have found any technical application as yet. Its composition, according to an analysis made in my laboratory, is:—

Sulphur	50·46	(of this 0·05 as lead sulphate in the insoluble residue).
Iron	44·55	
Lead	0·37	
Lime	1·13	
Magnesia	0·11	
Carbonic acid	1·01	
Silica, Iron peroxide, Alumina	1·70	(insoluble).
Moisture	0·40	
	99·73	

In *Poland* pyrites occurs together with blende, containing some thallium (Antiporo, Fischer's Jahresb. 1897, p. 421).

In *Belgium* a rich pyrites is met with, the great friability and softness of which do not tell in its favour. The following are analyses of this pyrites:—

	a.	*b.*	*c.*	*d.*	*e.*	*f.*
Sulphur	42·80	35·50	46·20	45·01	50·00	45·60
Iron	36·70	38·60	40·50	39·68	43·61	38·52
Ferric oxide	7·23	4·24	2·20			
Oxygen in ferric oxide	......	......	......	0·32	0·18	6·00
Lead	0·92	0·65	0·41	0·37		
Zinc	0·40	5·26	0·22	1·80	1·75	
Arsenic	0·20	0·31	0·41	trace	trace	trace
Thallium	......	......	......	trace		
Alumina	trace					
Silica	8·86	14·90	9·10	12·23	2·85	9·00
Carbonic acid	......	......	......	......	0·73	
Calcium carbonate	0·84	trace	......	......	......	0·11
Lime	......	......	......	0·25	0·92	
Water	1·46	0·56	0·42	0·25	0·10	0·36
	99·41	100·02	99·46	99·91	100·14	99·59

(*a*, *b*, and *c* by Clapham in Richardson and Watts's 'Chemical Technology,' vol. i. part iii. p. 14; *d*, pyrites from Rodieux near Spa; *e*, from Santon's pit on the Meuse, both by Pattinson, *l. c.*; *f*, by MacCulloch, Chem. News, xxvii. p. 125.)

The Belgian pyrites is usually only got as a by-product in obtaining lead- and zinc-ores in the provinces of Liège and Namur; it is either microcrystalline or crystalline or in bulbous pieces with a concentrically fibrous structure. Its quality is uneven. It is mostly used locally and in the north of France.

In 1860 as much as 42,513 tons of pyrites was got, but this was the maximum attained. In 1879 still 15,577 tons were procured, but in 1880 only 7913 tons, and in 1881 2965 tons. The production remained about 2000 or 3000 tons for a number of years, but since 1898 it has been altogether insignificant.

In *France* the principal deposits of pyrites are those of the Rhone (Chessy and Sain-Bel) and of the South (Gard and Ardèch). The Rhone beds exist on both banks of the Brevenne, a tributary of the Saone, on a width of 4 or 5 miles. The bed on the left bank is that of Chessy, about 6 miles long and several yards thick. This pyrites is bright yellow, very crystalline and friable. When first got it contained 4 or 5 per cent. of copper; but the cupreous vein has run out, and the non-cupreous ore on this side has nearly ceased to be worked. The beds on the right bank are those of Sain-Bel or Sourcieux. The northern part furnishes a more compact ore than that from Chessy. Most of it is non-cupreous, but there is also a vein with 4 or 5 per cent. copper; the gangue is mostly sulphate of baryta. Much more important is the southern part of this bed, the "masse de Bibost." The ore is here very rich in sulphur, green with yellow reflexion, and very friable, so that there is almost as much smalls as lumps; the gangue is almost entirely siliceous. The beds in the South of France are more numerous, but much less important. The most considerable mine is that of Saint-Julien-de-Valgalgues, in the Département du Gard; there is another mine at Soyons, in the Ardèche. The other French mines are of little importance. A detailed description of the French pyrites-mines has been given by Girard and Morin (Compt. rend. 1875, lxxxi. p. 190; Annales de Chimie et de Physique, [5] vii. p. 229); from this paper the following analyses are extracted, which seem more trustworthy than those

	Chessy.		Sain-Bel.				Masse de Bibost.	
	Lumps.	Smalls.	Non-cupreous.	Cupreous.	55 metres underground. I.	55 metres underground. II.	50 m. underground.	115 m. underground.
Sulphur	47·34	48·57	46·62	37·89	47·1	47·98	53·89	52·49
Iron	41·72	43·20	39·07	29·92	40·5	41·11	46·46	46·43
Copper	0·05	trace	...	4·61	...	...	...	...
Zinc	...	...	...	6·36	...	...	...	...
Arsenic	0·02	trace	0·05	0·06	trace	trace	slight trace	slight trace
Gangue	10·79	4·71	13·92	21·25	12·4	10·78	0·37	0·90
Moisture	0·08	3·52	0·17	0·09	...	0·20	0·04	0·04

	Saint-Julien.				Soyons.
	Outcrop (picked).	32 metres underground.	50 metres.	87 metres.	
Sulphur	49·11	44·13	42·87	41·13	43·94–49·68
Iron	43·24	38·24	37·94	36·85	39·15–43·04
Arsenic	0·11	0·05	0·10	0·08	0·16– 0·39
Calcium carbonate	2·55	5·52	2·86	9·69	.
Magnesium carbonate	trace	trace	trace	0·08	...
Calcium sulphate	...	...	...	...	0· – 1·67
Calcium fluoride	1·09	trace	trace	trace	trace– 0·63
Insoluble	2·48	10·20	13·19	11·23	4·15–11·76
Oxygen in excess	...	...	1·40	0·38	0· – 1·02
Moisture	1·33	1·74	1·59	0·57	0·86– 4·58

by Mène, given in the 1st edition of this book, p. 92, from the Monit. Scient. 1867, p. 410.

These analyses may be summed up as follows:—The pyrites from the Rhone and Sain-Bel, on an average, contains 46 to 48 per cent. of sulphur and 10 to 12 per cent. of gangue, consisting of clay, sand, and barytes. In the southern part of the district of Sain-Bel the percentage of sulphur rises to 50 or 53, and the gangue is inconsiderable and free from barytes; arsenic is not present in quantities sufficient for determination. In the district of St. Julien (Le Gard) pyrites is not found in the clay-slate, as at Sain-Bel, but in the Lias or Trias; the sulphur varies from 40 to 45 per cent.; the gangue is calcareous, and varies from 3 to 6 per cent.; arsenic is present up to 0·1 per cent., sometimes also fluorspar in quantities sufficient for estimation. The pyrites from Ardèche contains from 45 to 50 per cent. of sulphur; the gangue is clay, free from lime; arsenic occurs up to 0·3 per cent.: fluorspar sometimes occurs in injurious quantities; the hydrofluoric acid given off from it in one case destroyed the glass apparatus for spreading the nitric acid, and the latter thus got to the chamber-bottom and corroded it.

In 1874 there were used in France 178,400 tons, of the value of £240,000. Of this the beds of Sain-Bel, which supply two-thirds of the French factories, contributed 120,000 tons, those of St. Julien (in the department Gard) 24,600 tons, those of Le Soulier (Gard) 6000 tons, those of Soyons (Ardèche) 900 tons. Girard and Morin give twenty-three analyses of French and five of foreign pyrites used in France.

According to Scheurer-Kestner (Wurst, Dict. de Chimie, ii. p. 138) the pyrites from Chessy and Sain-Bel contains 45 to 48 per cent. of sulphur with very little arsenic and selenium, that from Chessy also 1 or 2 per cent. of copper and zinc. The copper is obtained from the cinders, at least at the Chessy works, by allowing them to lie for a time and moistening them: the liquid running off contains copper and zinc sulphates; and the copper is got from it by cementation. Nearly all French works, as well as those in Alsace and Switzerland, obtain their ore from those two pits; only the works at Gard and Marseilles get it from Alais, where the pyrites contains 38 to 42 per cent. of sulphur; a few factories in the north of France use Belgian pyrites, those in the south use Spanish pyrites.

The production of pyrites in France was :—

1891.	243,030 tons.	1896.	295,325 tons.
1892.	226,304 „	1897.	298,571 „
1893.	227,288 „	1898.	306,002 „
1894.	278,452 „	1899.	313,087 „
1895.	248,934 „		

France imported and exported pyrites as follows :—

1890.	Imported	39,552 tons.	Exported	15,907 tons.
1891.	„	45,457 „	„	12,120 „

Italy possesses beds of pyrites in several places. Those occurring in the province of Bergamo, tested in Vienna (Wagner's Jahresb. 1879, p. 272), are composed as follows :—

	Redolta quarry.	Passevra quarry.	S. Guiseppe pit.	Vallantica pit.
Iron	36·29	41·72	48·35	36·79
Copper	trace	trace	0·07	1·69
Zinc	trace	...	0·18	...
Lead	...	...	...	trace
Silver	...	...	...	0·014
Sulphur	39·32	44·36	30·97	41·56
Arsenic	0·53	0·14	...	0·18
Alumina	2·37	1·28	1·86	1·25
Lime	5·89	0·88	1·70	0·37
Magnesia	0·66	0·39	0·14	0·10
Silica	7·16	9·68	10·45	16·40
CO_2, O and H_2O (by diff.)	7·78	1·55	6·28	1·646
	100·00	100·00	100·00	100·00

In the Val d'Aosta there are several mines, some of which contain a strongly arsenical pyrites.

Those at Brosso, near Ivrea, belonging to Messrs. Sclopis & Co., yield pyrites containing very little arsenic : present output about 20,000 tons per annum. One quality contains 48 or 49 per cent. of sulphur and 0·2 of arsenic, the other nearly 50 of sulphur and only traces of arsenic. It is too explosive for burning in lumps, but excellent for burning as smalls. Another mine is at Pré St. Didier in the same valley. This Aosta pyrites mostly requires special contrivances for getting rid of the arsenic in burning; the cinders are worked for copper, silver, and gold.

Pyrites in quantity is also found at Agordo (Cadore), Sestri Levante, and of very good quality in Sicily. The whole of the 24 Italian sulphuric-acid works burn pyrites, partly imported from Spain (Candiani, Chem. Ind. 1895, p. 153); none of them burn brimstone.

The production of pyrites in Italy was:—

1897	57,383 tons.
1898	66,120 „
1899	75,308 „

Swedish pyrites, from Fahlun, varies between 43 and 48 per cent. of sulphur. This ore is obtained as a by-product in the getting of copper-ores, and is said to exist in enormous quantity; but, owing to the difficulty of transit, its exportation does not pay. It is said to burn well.

	Pattinson.	Browell and Marreco.
Sulphur	43·70	38·05
Iron	39·01	42 80
Copper	0·60	1·50
Lead	0·12	
Zinc	2·57	
Lime	0·85	
Magnesia	0·69	
Arsenic	trace	
Insoluble	11·66	12·16
Oxygen, as Fe_2O_3.........	0·22	Oxygen and loss } 5·49
Water	0·20	
	99·62	100·00

In *Norway* there exist very large beds of pyrites, both free from and containing copper. Of the many pits formerly worked there, all those had to stop which produce ores with from 35 to 40 per cent. of sulphur. The richer ores, even those free from copper, have maintained their position to some extent, because they burn well, are easily lighted, keep the heat well, do not "scar," &c. They are mostly hard and difficult to break. The most considerable pits are those of Ytteröen, which export *viâ* Drontheim; they supply 6000 to 8000 tons per annum. A large mass of cupreous pyrites, with 45 per cent. of sulphur and 3 of copper, at Vigsnaes, was worked by an Antwerp Company, but is now exhausted. Norwegian pyrites contains very little arsenic. Other pits exist thirty miles from Drontheim, on the Hardanger Fjord, near Bergen, &c. The Norwegian pyrites is more in favour as a sulphur-ore (excepting its difficult breakage) than as a copper-ore; its cinders do not very well suit the copper-works.

Analyses of Norwegian Pyrites.

	Pattinson.		MacCulloch.	
	Ytteröen ore.	Drontheim ore.	I.	II.
Sulphur	44·50	50·60	46·15	38·17
Iron	39·22	44·62	44·20	32·80
Copper	1·80	trace	1·20	1·10
Zinc	1·18	1·34	2·10	2·32
Lead	...	trace	...	...
Lime	2·10	trace	...	...
Calcium carbonate	...	...	2·55	11·90
Magnesia	0·01	trace	...	...
Magnesium carbonate	...	...	...	1·08
Carbonic acid	1·65	...	...	...
Arsenic	...	...	...	trace
Insoluble	9·08	3·15	3·20	12·20
Oxygen, as Fe_2O_3	0·45	...	...	...
Moisture	0·17	0·20	0·40	0·25
	100·16	99·91	99·80	99·82

The following information is due to Mr. Knudsen, manager of the Sulitjelma mine (through Dr. Hasenclever). Norway exported in 1901 about 90,000 tons pyrites from the following pits:—

Sulitjelma, near Bodoe	35–36,000	tons with	45 p.c.	sulphur.
Killingdal	25,000	„	43–44 p.c.	„
Röros, near Trondhjem	15,000	„	43–44 „	„
Bossmo „	15,000	„	48–50 „	„

By far the largest mine is the first-mentioned, which is expected to yield an additional 20,000 or 25,000 tons in 1902 and is reckoned to last for centuries to come. It contains very little arsenic. Much ore, richer in copper and poorer in sulphur, is also smelted on the spot. The ore from Killingdal and Röros is also cupreous; that from Bossmo is free from copper, with traces of arsenic. The following mines are not yet worked for want of railway communication:—Foldal, Vaarteigen, and Nudal. They test 43 or 44 per cent. S, and at most 2·5 per cent. Cu, and might yield from 60,000 to 90,000 tons per annum.

Spain and Portugal possess the largest known beds of pyrites. Much of it is cupreous, and all of it is distinguished by its very good behaviour in burners; so that the burners have been built very much lower for it, and much labour is saved. This pyrites has only been worked again since 1855; but the Romans, and before them the Phœnicians and Carthaginians, knew it very well, as is shown by many traces. The bed, however, was at that time only worked where it was richest in copper. According to Schönichen (Dingl. Journ. clxx. p. 448) all the beds are within a belt of five leagues width, reaching, parallel to the Sierra Morena, from the western frontier of the province of Seville, across the hilly country situated to the south of this, right through Portugal to the Atlantic Ocean—a distance of 30 leagues. The prevailing rocks in that country are clay-slate and crystalline slates; but parallel to the granitic tract of the Sierra Morena felsite-porphyry and quartzite have broken through the slate, and only in the neighbourhood of such dykes are the pyrites-beds found. Their shape is that of large lenticular pockets in the metamorphic clay-slate, from 20 to 36 fathoms thick, and extending to a length of 170 to 260 fathoms. The whole bed is filled with pure pyrites, without any visible gangue. The ore is in a few places found at only 1 or 2 fathoms below the surface, undecomposed, and in a sandy state, so that it can be got by daylight work. In other places the zone of decomposition reaches from 10 to 50 fathoms downwards. The percentage of copper varies from 2½ to 40; but ores with more than 10 per cent. of copper are only contained in small vertical zones within the large masses. Only these "black" ores were the object of the mining-operations on the part of the Phœnicians and Romans. The quantity of pyrites existing there is almost inexhaustible, and can certainly supply the requirements of mankind, both of copper and of sulphur, for thousands of years to come.

Special highways, and latterly also railways, have been made, in order to facilitate the communication with the ports of Huelva, San Lucar du Guadiana, and Pomaron; but a great deal of the ore is still conveyed for some distance on mule-back.

Of the many companies which had been formed for working this ore most have ceased to exist; and only four or five remain, all of them in English and French hands. The smallest of these is the Buitron Pyrites Company, which works the mines of Buitron and Poderosa. The Tharsis Sulphur and Copper Company possesses much more extensive mines, a railway of its own, a wharf at Huelva, and also a number of works in England and Scotland for the wet extraction of the copper from the cinders returned to them. The Tharsis ore is very good, but very soft, and makes much dust in breaking. The San-Domingo mine lies in Portuguese territory; its ore is known as Mason's ore, and is considered superior to all others, so that it commands a better price. The last, but largest, of these companies is the Rio-Tinto Company, which has thrown such large quantities of pyrites into the English market that, from 1875 to 1876, prices receded by more than one-third. Its ore is also of excellent quality. The mines of Carpio and Lagunazo, in the province of Huelva, are not yet worked for exportation.

The Spanish (and Portuguese) pyrites never contains less than 46, and up to 50 per cent. of sulphur, besides 3 to 4½ per cent. of copper, which, however, by most of the English buyers, is not bought, but returned in kind to the seller in the shape of cinders from the pyrites-burners. The value of the copper (if bought) is still fixed by the so-called "Cornish assay"—that is, a process of dry assaying known only to a few assayers living at Redruth and other places in Cornwall, the great inaccuracy of which is perfectly well known to all parties concerned: it shows, for instance, only 2 per cent. if 4 per cent. is actually present; and from this difference the buyer must pay the cost of extracting the copper and his own profit, since the price to be paid for the copper *in the ore* by Cornish assay is sometimes higher than the value of a similar quantity of copper *metal.* This remarkably irrational system has not hitherto been done away with for sales.

In Germany also in 1877 a number of manufacturers united in working Spanish pyrites (especially Rio-Tinto ore), and in delivering all their cinders to the Duisburg copper-works. The Oker works also use similar ores, which they work up themselves for copper.

The ore of the three principal companies is very similar in composition; its analysis is as follows:—

	Pattinson.				Claudet (San Domingo ore).	MacCulloch (San Domingo ore).
Sulphur	48·00	49·60	44·60	49·30	49·00	49·80
Iron	40·74	42·88	38·70	41·41	43·55	42·88
Copper	3·42	2·26	3·80	5·81	3·20	2·26
Lead	0·82	0·52	0·58	0·66	0·93	...
Zinc..................	trace	0·10	0·30	trace	0·35	0·10
Lime	0·21	0·18	0·14	0·14	0·10	0·18
Magnesia	0·08	trace	trace	trace	...	...
Thallium............	trace	trace	trace	trace	...	...
Arsenic	0·21	0·28	0·26	0·31	0·47	0·28
Insoluble	5·67	2·94	11·10	2·00	0·63	2·94
Oxygen (as Fe_2O_3)	0·09	0·15	0·23	0·25	1·07	...
Moisture............	0·91	0·95	0·17	0·05	0·70	0·95
	100·15	99·86	99·88	99·93	100·00	99·39

The following analyses represent the average quality :—

	Rio Tinto.			S. Domingo.		
	Cumenge.	Caron.	Rivista Min. 23.	Pattinson.	Bartlett.	Tharsis. Bartlett.
Sulphur	48·00	50·7	49·00	49·90	49·80	47·50
Iron	40·00	41·3	43·55	41·41	43·55	41·92
Copper	3·42	3·5	3·20	2·46	3·20	4·21
Lead	0·82	...	0·93	0·98	0·93	1·52
Zinc..................	trace	...	0·35	0·44	0·35	0·22
Arsenic	0·21	...	0·47	0·55	0·47	0·38

Jurisch (Schwefelsäure-fabrikation, p. 30 *et seq.*) quotes further analyses. In 1879 the sulphur in Rio-Tinto ore averaged 48·55 per cent., varying between 48·18 and 48·77 per cent. S.

A new pyrites-mine has been opened in Spain, called St. Mardy Tinto Santarossa. Its product has been found by Lunge and Bänziger (Zeitsch. angew. Chem. 1896, p. 421) to contain 0·85 per cent. moisture, 5·20 insoluble, 43·87 sulphur, 42·12 iron, 1·09 arsenic, 2·15 antimony, 3·17 copper.

Some kinds of Spanish pyrites are in bad repute with the manufacturers as "explosive" or "detonating," because they decrepitate in the kilns shortly after lighting with loud detonations, and thereby make so much fine powder that the burners are stopped up and "scars" are formed. The reason of this detonating property is probably to be sought in the presence of hydrated silicates (zeolites) in the ore *.

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* The explosive pyrites from Goshen Copper Mine, near Scull Harbour, County Cork, is said to contain confined carbon dioxide and water (Blount. J. Soc. Chem. Ind. 1885, p. 674).

According to Hjelt the average percentage of arsenic in Spanish ores is 0·91.

Pyrites with very little or no copper is also found in Spain. One of the best descriptions is that of the Agnas Teñidas mine, containing iron 46·60 per cent., sulphur 53·15 per cent., silica 0·20 per cent., arsenic, copper, selenium, silver and gold traces. It is sold both in the state of lumps and smalls. It burns very easily down to 1·0 or 0·5 per cent. of sulphur, so that the cinders, which contain 68·5 per cent. of metallic iron, and no copper, phosphorus, lead, or zinc, are very valuable for blast-furnaces. The annual sales have exceeded 200,000 tons, but recently very little has come into the market owing to an accident at the mine.

H. J. Davis of New York, one of the principal importers of pyrites to the U.S., gives the following analyses of very good, hard Spanish ores containing but little copper:—

	Aracena.	Balmacca.	San Tolmo.
S	51·77	50·19	46·40
Fe	45·53	45·61	40·11
Cu	0·29	0·20	1·90
Si	1·90	3·00	11·27
As	?	?	none

The production of iron-pyrites (non-cupreous) in Spain, according to 'United States Mineral Resources' for 1900, p. 826, was as follows:—

1891.	279,161 tons.	1896.	98,393 tons (?).
1892.	435,906 ,,	1897.	217,545 ,,
1893.	393,453 ,,	1898.	255,896 ,,
1894.	511,769 ,,	1899.	316,212 ,,
1895.	480,255 ,,		

The production of cupreous pyrites and its exportation by the three principal firms in Spain and Portugal was, according to the same authority, p. 186:—

1. Rio Tinto Company.

1898.	Production	1,465,380 tons	(2,852 p.c. Cu).
1899.	,,	1,649,844 ,,	(2,719 ,, ,,).
1900.	,,	1,894,504 ,,	(2,744 ,, ,,).

Exportation in 1900: 704,803 tons.

2. Tharsis Sulphur & Copper Co.

1899.	Production 572,854;	exportation 222,475 tons.
1900.	„ 468,738;	„ 220,019 „

3. Mason & Barry, Ltd. Exported :

1899. 339,298 tons.
1900. 394,740 „

Enormous quantities of cupreous pyrites are roasted and worked for copper in Spain, without utilizing the sulphur, as is apparent from the above figures.

The *United States of North America* are very rich in pyrites. The principal mines worked at present are the following:—

In New Hampshire: the Milan mines, Coos County. The ore is of excellent quality, and is now sorted into two grades, of the following composition:—

	No. 1.	No. 2.
Sulphur	46·0	35·0
Copper	3·7	5·0
Iron	40·0	30·5
Silica	6·2	25·5
Zinc	4·0	8·0
Arsenic	0	0

No. 1 is in special favour, but No. 2 burns very well and is readily bought. Smelting-works exist for extracting the copper and silver.

New York: 2000 tons were raised at Hermon, County St. Lawrence; sulphur contents, 38·0 per cent. Another mine at Ulster County, with 39 per cent. ore, was worked till stopped by an inrush of water.

Massachusetts: the mines of the Davis Company, at Charlemont (Mass.), are about 130 miles from New York, in the centre of a network of railways. The ore contains 48·5 per cent. sulphur, no trace of arsenic, antimony, or cobalt, little or no zinc, lead, or calcium, 1·5 copper, 45·3 iron, and less than 3 per cent. of silica. It is granular, easily broken by hand, and burns down to 3 per cent. of sulphur. In 1884, about 30,000 tons were got; it was burned in four works.

Virginia: Arminius Copper Mines Company and Sulphur Mines Company, both in Louisa County. The ore contains 49·5 per cent.

sulphur, 0·5 copper, 43·5 iron, 6·4 silica, &c. Annual output, 13,000 tons (in 1885).

Georgia: Dallas mine, Paulding County. The ore contains: sulphur 40 per cent., copper 2·75 (sometimes up to 11 per cent.), silica 8 per cent.

The absence of arsenic in most American pyrites (as far as it is now worked) is a remarkable feature.

K. F. Stahl (Zsch. f. angew. Chem. 1893, p. 54) quotes analyses of American pyrites. No. 1 is from Tallapoosa Mine, Georgia, 1882; No. 2 from Rogers Mine, Paulding Co., Dallas, Ga.; No. 3 from Sulphur Mines Co. of Virginia, Louisa Co., 1884; No. 4, Peru Zinc Co., La Salle, Ill.; No. 5 from Dodgeville, Wis.; No. 6, from the same mine as No. 3, 1891; No. 7, Davis Sulphur Ore Co., Franklin Co., Mass., 1891.

	1.	2.	3.	4.	5.	6.	7.
Water	—	—	2·9	—	—	1·3	0·8
Sulphur.........	45·1	37·6	37·1	50·2	43·7	40·6	42·4
Iron	—	40·6	41·5	—	—	37·3	35·4
Copper	3·1	5·2	0·6	—	—	1·0	1·4
Zinc	3·0	4·5	0·8	—	—	1·9	5·5
Cadmium	0·1	0·01	?	—	—	?	?
Insoluble	2·9	9·5	14·7	—	1·4	10·5	5·1
Arsenic	?	?	0·02	—	—	trace	trace

We quote from the volumes of 'Mineral Industry' the production, imports, and consumption of pyrites in the United States, not counting the auriferous pyrites used for the manufacture of sulphuric acid in Canada, expressed in long tons of 2,240 lbs.:—

Year.	Production.	Imports.	Consumption.
1891	100,319	130,000	239,319
1892	106,250	210,000	316,250
1893	95,000	194,000	289,000
1894	107,462	146,023	253,485
1895	81,000	190,436	271,436
1896	109,282	199,678	308,960
1897	133,368	259,546	392,914
1898	191,160	171,879	363,039
1899	178,408	310,008	488,416
1900	201,317	329,449	530,766

Most of the American pyrites, including the Newfoundland ore, is granular and more fit for fines' burners than for lump-burners.

In *Canada* there are two mines: the Albert mine and the Crown mine. They supplied the first pyrites used in the United States for making oil of vitriol. Sulphur 40·0 per cent., iron 35·0, copper 4·0, silica 20·0. Output:

1891.	60,474 tons.	1894.	36,185 tons.	1897.	34,471 tons.
1892.	53,372 „	1895.	30,534 „	1898.	24,721 „
1893.	52,270 „	1896.	30,103 „	1899.	35,742 „

In *Newfoundland*, on Piney's Island, there is a very large bed of pyrites, accessible by a shaft 60 feet deep. The bed is 72 feet wide, and 28 feet of it contains 3 or 4 per cent. copper. This ore is very easy to roast; an analysis of the non-cupreous ore showed Cu 0·07, S 51·16, Fe 48·35, SiO_2 0·13, CaO 0·22, As 0·02; no Sb, Pb, Zn, Bi (Eng. Min. Journ. 1892, p. 467).

In *South Australia* pyrites is found with 48·7 per cent. S and 2·8 per cent. Cu (Mène, Mon. Sc. 1867, p. 411).

The World's production of iron-pyrites (in metric tons) is stated in Min. Ind. ix. p. 615, from official sources (I cannot explain the difference between these and the other "official" figures given in various places *suprà*):—

	1895.	1896.	1897.	1898.	1899.
Belgium	3,510	2,560	1,828	147	283
Bosnia	...	2,000	3,670	240	430
Canada	31,024	30,586	35,299	29,228	25,117
France	253,416	282,064	303,448	310,972	318,832
Germany	127,036	129,168	133,302	136,849	144,623
Hungary	69,195	52,697	44,454	58,079	79,519
Italy	38,586	45,728	58,320	67,191	76,538
Newfoundland	34,879	27,712	33,316	33,100	31,500
Norway	61,994	60,507	94,484	89,763	90,000
Portugal (*a*)	200,000	200,000	210,265	248,218	275,658
Russia	11,042	11,550	19,380	20,000	25,000
Spain (*b*)	60,267	100,000	217,545	260,016	319,285
Sweden	221	1,009	517	386	150
Great Britain	9,193	10,178	10,753	12,302	12,426
United States	107,371	117,782	128,468	194,219	181,263
Totals	1,007,734	1,073,541	1,295,049	1,460,710	1,580,624

(*a*) For Portugal the output for 1895 and 1896 is roughly estimated. For this country only pyrites with less than 1 per cent. copper is included.

(*b*) For Spain the cupreous pyrites, from which copper is extracted, is not included, comp. p. 57.

Average Composition of the World's Pyrites.

(From 'United States' Mineral Resources,' 1886, p. 652.)

Localities.	Sulphur.	Iron.	Copper.	Arsenic.	Zinc.	Lead.	Carbonate and Sulphate of Ca and Mg.	Silica.
Milan mine, New Hampshire, No. 1	46·00	40·00	3·75	trace	4·00	none	...	6·25
" " No. 2	35·00	30·50	5·00	none	8·00	...	...	21·50
Davis mine, Mass.	49·27	45·30	1·47	trace	...	...	...	3·83
Elizabeth mine, Vermont	33·00	50·00	3·50	...	...	...	...	13·50
St. Lawrence Company, New York.	38·00	34·00	3·00	...	...	...	...	25·00
Arminius mine, Va.	46·00	44·50	2·10	...	...	...	...	7·40
Capelton, Canada	40·21	35·20	5·10	trace	...	...	8·00	12·00
Rio Tinto, Spain	48·50	40·92	4·21	0·33	0·22	1·52	0·90	3·46
Tharsis, Spain..........	49·90	42·55	3·10	0·47	0·35	0·93	0·87	2·20
S. Domingo, Portugal	49·07	44·28	3·25	0·38	...	...	0·93	2·59
Swedish mines..............Average	38·05	42·80	1·50	none	...	...	5·09	12·56
Norwegian " .... "	46·15	44·20	2·10	trace	1·20	...	2·50	3·65
French " .... "	46·60	39·70	none	...	...	...	0·20	13·50
German " ... . ,	45·60	38·52	...	0·95	6·00	0·74	...	8·19
Belgian " .... "	42·80	36·70	...	0·20	0·40	0·92	5·45	12·47
English " .... "	34·34	32·20	0·80	0·91	1·32	0·40	...	30·03
Irish [?] " .... "	47·41	41·78	1·93	2·11	2·00	...	...	4·77

Prices obtained in the Liverpool district for pyrites, when sold for sulphur only:—

Year.	Prices per unit of sulphur.	Year.	Prices per unit of sulphur.
1861	10·85*d.*	1870	6½*d.*
1862	9·625	1871	7¼
1863	8	1872	7½
1865	9	1873	7½
Jan. 1866	9½	1876	5½
Mar. 1866	11·02	1877	4½
Jan. 1868	10·04	1878	4½
June 1868	9½	Jan. 1879 to Dec. 1884	5¾
Oct. 1868	8		
Jan. 1869	7	1885 to 1887	3 to 3½
June 1869	8		

(E. K. Muspratt in J. Soc. Chem. Ind. 1886, p. 405.)

Jurisch (Schwefelsäure-fabrikation p. 58) quotes the prices of pyrites in Germany from 1853 to 1892; but this is of very little use, as there is nothing said about the percentage of sulphur. Previous to 1883 the price was always above 10 marks per ton, from 1884 to 1892 it ranged about 7½ marks per ton. Only one definite statement is made, viz. that 100 kil. of sulphur actually burned from Rio Tinto, deducting the drawback for copper, in 1881 cost 4·65 to 5·10 marks (?).

In 1900, the ordinary price of German pyrites was 12 marks per ton at the mine; for large contracts probably less.

Proportional value of poor and rich Pyrites.

It is no matter of surprise that the rich and at the same time well-burning Spanish ores, and those ores similar to them elsewhere, where they could be imported, have driven the poor ores out of the field. An ore of 35 per cent., like that from Wicklow, even for the same weight of sulphur, has much less value than a 45-per-cent. ore. The wages for breaking and burning the ore in both cases must be ruled by the gross weight of the ore, and consequently for equal weights of sulphur come to much more with poor than with rich pyrites; moreover, under conditions otherwise equal, the unburnt sulphur in the cinders is the same by weight. If, for instance, 5 per cent. of sulphur are left in the cinders, this amounts with 35-per-cent. ore to $\frac{5}{35}=\frac{1}{7}$; with 45-per-cent. ore to only $\frac{5}{45}=\frac{1}{9}$; the proportion to be kept in view is accordingly not 35 : 45 = 7 : 9, but 30 : 40 = 3 : 4. Furthermore, the same holds good of cost of plant and repairs and of wages, and, lastly, since the poor ores generally contain no copper, also of the cost of removing the cinders.

Therefore, unless the burning is nothing but a preparation for the metallurgical treatment, where the sulphur is quite of secondary importance, the ores poor in sulphur are always avoided as much as possible.

Analysis of Pyrites.

In the analysis of pyrites for technical purposes, in the first instance their percentage of sulphur is taken into account; and it is therefore mostly the custom to estimate only this and, perhaps, also the moisture. If the ore has afterwards to yield copper, this must of course also be considered; but where the copper, as is mostly the case, is not bought by the vitriol-maker, but the cinders are returned to the seller, the estimation of copper is generally omitted in the chemical works as unnecessary. This restriction to the estimation of sulphur ought, however, only to take place with pyrites from well-known localities, whose general composition and properties are well known, and where the salient point is only the percentage of the most important constituent, viz. the sulphur. Each cargo, even each portion of a cargo going to a separate buyer, is sampled in the presence of both the buyer's and seller's agents, according to well-understood rules: the sample is broken up, reduced, and sealed up in bottles, which are sent to an analytical chemist (generally mentioned in the contract note); this chemist's certificate rules the price to be paid for the pyrites down to ¼ per cent. If, for instance, a sale has been made at 6*d.* per "unit," this means that for each per cent. of sulphur found the sum of 6*d.* per ton is paid; thus for 48¼ per cent. of sulphur 48¼ × 6*d.* = 24*s.* 1½*d.* per ton. The ton is generally calculated = 21 cwt.; that is to say, the buyer receives an allowance in weight of 5 per cent.

The first treatment of the pyrites in analyses, in the majority of cases, is by the *wet* way, by fuming nitric acid or aqua regia; but the prescriptions differ in details. The decomposition was formerly frequently made, from Fresenius's prescription, by means of red fuming nitric acid, which it is sometimes difficult to obtain free from sulphuric acid, and which is unpleasant to handle. In lieu of this sometimes chlorate of potash along with hydrochloric acid, or, still better, with nitric acid of 1·36 sp. gr., have been used. The author has always found the best, safest, and cheapest way to be that by aqua regia, made from 1 part of fuming hydrochloric acid and 3 or 4 parts of nitric acid of 1·36 to 1·4 sp. gr., and this mixture is now used in most places. The mineral is converted into an impalpable powder and passed through the finest silk gauze; the triturating ought to be done first in a steel mortar or by wrapping it up in paper and smashing with a hammer, and then in an agate mortar, *not* in a porcelain or Wedgwood mortar. The powder is treated with about 50 parts of aqua regia; if no reaction takes place at once, it should be gently heated on a water-bath till the reaction sets in; but then the beaker should be removed instantly from the water-bath, and only replaced when the reaction slackens: thus the decomposition is generally complete in 10 minutes. The operation should be performed in a large beaker, or, still better, in an Erlenmeyer's flask covered by a funnel or a watchglass, lest any loss should take place by spurting; and the work must be done in a draught-place, on account of the mass of acid vapours given off. If the decomposition should not be perfect after heating some time, some more aqua regia has to be added and the heating continued; but mostly this will be caused by the powder not being sufficiently fine, and the analysis in this case cannot easily be finished. In this way of decomposing the ore, which is both quick and safe, the disagreeable separation of sulphur happens very rarely. If it does, the sulphur is oxidized by cautiously adding a little chlorate of potash.

The residue from the solution will contain silica and silicates, perhaps a little lead or barium, both as sulphates. Although their sulphur is thus not estimated, no harm is done, as it is anyhow valueless to the manufacturer. Lead sulphate is pretty soluble in concentrated acids, but it is almost entirely precipitated again by the immediately following treatment.

At all events the whole of the nitric acid present must be destroyed or removed, because the estimation of sulphuric acid by barium chloride in the presence of nitric acid or its salts gives results much in excess of the truth. The whole is therefore evaporated to dryness on the water-bath * with an excess of hydrochloric acid, by which at the same time all silicic acid dissolved is made insoluble. The mass is again moistened with strong hydrochloric acid; and if on gently heating no yellow vapour and no smell of nitrous products are perceived, it is diluted with hot water and the solution filtered from the residue. Care must be taken not to employ too much hydrochloric acid, as barium sulphate is not quite insoluble in hot concentrated acids; on the other hand, enough acid must be present to dissolve all salts of iron, which cannot be doubtful if the colour and behaviour of the residue are observed.

Some chemists prefer to the aqua regia above described a solution of bromine in hydrochloric acid; but I have not found this to answer very well. Drown (Chem. News, xliii. p. 89) heats the pyrites with a solution of caustic soda of spec. grav. 1·25, adds cautiously bromine in excess, acidulates with hydrochloric acid, and evaporates to dryness.

Noaillon (Zsch. angew. Ch. 1897, p. 351) employs a mixture ot sodium chlorate and nitric acid for decomposing the pyrites, in order to avoid loss of sulphuric acid when drying the resulting mass. (Such a loss never occurs when working according to my prescription.)

Where the utmost accuracy is not desired the solution may now be at once treated with barium chloride, as follows:—

The clear solution is brought to *full boiling*; and to it during boiling a *hot* solution of barium chloride is slowly added. Lest too great an excess of this be used, it is preferable to use a measured quantity of a concentrated solution of known strength, but more than sufficient for precipitating all the sulphuric acid present. It is best to pour the hot solution of barium chloride rather slowly into the boiling solution of sulphate, with constant stirring, but it is quite unnecessary to do this drop by drop as prescribed by Gladding (Chem. News, lxxx. p. 181); comp. Lunge, Zsch. ang. Chem. 1895, p. 69, and Journ. Amer. Chem. Soc., March 1895. If the process is carried out as described here, the barium sulphate settles down completely in a few seconds, leaving a perfectly clear liquid, and nothing of the

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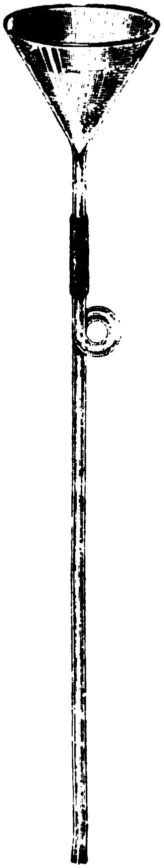
* The last evaporation may be hastened by employing a sand-bath or asbestos cardboard, taking care to remove the vessel at the moment when the mass has become dry.

precipitate passes through the filter. It is quite unnecessary to allow a long time for the settling. If the operation is carried on as described, the filtrate never becomes cloudy afterwards; on the other hand, the work is greatly expedited by filtering the liquid in the boiling-hot state, say 15 or 20 minutes after precipitation. A Bunsen's filter-pump acts rather too strongly in this case; but it is very useful to employ a simple contrivance indicated many years ago by Piccard, which does excellent service in other analytical operations, viz., a glass tube attached to the funnel by means of an elastic joint, with a loop causing a continuous jet of liquid to issue at the bottom (fig. 5). The straight part below the loop may be 8 or 10 inches long; the filter must be pressed tight to the sides of the funnel to prevent any air being sucked in. When this contrivance is used, which does not act so violently as a Bunsen pump, the liquid, so long as there is not too much precipitate in the filter, runs through in a continuous jet.

Fig. 5.



At first only the clear liquid is poured off as completely as possible from the dense granular precipitate; this is covered with *boiling* water, acidulated with a few drops of hydrochloric acid; the liquid is boiled for a few moments, and can be decanted in about two minutes' time. This operation is again repeated twice or three times, but without adding any more hydrochloric acid; the precipitate is washed onto the filter, and after very little washing the filtrate will be found perfectly neutral and free from dissolved matters. The filter is dried, the precipitate taken out, and the filter burnt, preferably in a platinum crucible laid on its side; then the precipitate is put in and ignited, not too strongly: and for each 100 parts of barium sulphate found 13·733 parts of sulphur are calculated. The ignited barium sulphate must not cake together; on moistening, it should not give an alkaline reaction; and on heating with dilute hydrochloric acid and filtering, no barium salt ought to be found in the solution.

It generally happens, even if the solution before precipitation was rather strongly acid, that the precipitate is stained yellowish by precipitated ferric oxide or basic ferric sulphate, which cannot be removed even by boiling with dilute hydrochloric acid.

Although this proves the presence of a foreign substance in the barium sulphate, which ought to make the result too high, yet it is found in practice that the results are always too low. The cause of this apparent anomaly has been studied by Jannasch and Richards (Journ. f. prakt. Chem. [2] xxxiv. p. 321), who found that in the presence of iron a barium-ferric sulphate is precipitated, which on ignition slowly loses a portion of its sulphuric acid. If the ignition is carried on very persistently, the error thus produced may amount to a full per cent. of sulphur or upwards; but I have shown, in the paper quoted below, that with the ordinary mode of ignition it does not exceed 0·18 per cent.; hence the above-described method is always available where perfect accuracy is not required and a speedy completion of the test is a consideration. Westmoreland (J. Soc. Chem. Ind. 1887, p. 84) even contends that its results entirely agree with those obtained by my new method (an opinion to which I must demur).

Where, however, the greatest possible accuracy and freedom from error is required (and this is the case when testing an average sample of pyrites representing a whole cargo, or a large portion of such), it is necessary to remove the disturbing influence of the iron. This can be done in two different ways, by the *dry* and by the *wet* method. The *dry* method is that recommended by Fresenius (Zeitsch. f. anal. Chemie, xvi. p. 335). He prescribes to decompose the pyrites by fluxing it with 20 parts of a mixture of 2 parts of dry sodium carbonate entirely free from sulphate, and 1 part of potassium nitrate, passing carbonic acid into the solution for the precipitation of lead, boiling the residue with a solution of sodium carbonate and then with water, acidulating with hydrochloric acid, and repeatedly evaporating for the expulsion of nitric acid, after which the process is carried on as usual, the precipitation taking place by barium chloride. This process is much more troublesome and tedious than that to be described below, which employs the wet method. Another objection to it is that it estimates not merely the sulphur of the iron and copper sulphides, but also that of galena and of barium sulphate, which are entirely useless to the manufacturer of sulphuric acid*. Moreover, the platinum crucibles are strongly acted upon, and coal-gas cannot very well be employed in the operation of decomposing the pyrites, as its sulphur would cause an error in the test. Hence it is advisable to use spirit-lamps of a special shape, calculated to yield the necessary heat. [The use of spirit-lamps can be practically avoided by placing the crucible in a round hole made in a piece of asbestos cardboard, in which case the products of the combustion of coal-gas are carried off sideways.]

Hayes ('American Chemist,' v. p. 271) describes a method of decomposing pyrites with alcoholic soda and lime, the advantages of which are in no way evident.

Fahlberg and Iles (Ber. d. deutsch. chem. Ges. xi. p. 1187) recommend fluxing the sulphur-ore with caustic potash (25 grams to 0·1 gram of S) in a silver crucible for 15 to 20 minutes, lixiviating the mass, oxidizing the lower oxides of sulphur by bromine-water, and precipitating by barium chloride.

Clark (J. Soc. Chem. Ind. 1885, p. 329) heats the pyrites with a mixture of sodium carbonate and magnesia to a dark-red heat; the resulting mass is lixiviated with water whilst passing in carbonic acid, and the sulphuric acid estimated in the usual way. J. Pattison (*ibid.* p. 724) shows that this method gives exactly the same result as mine (of course, only in cases where barium sulphate and galena are absent, which militates against Clark's process).

Looking at the great desirability of retaining the decomposition of pyrites in the *wet* way, I have worked out a method for doing so without incurring the error caused by the presence of iron. This method was first described in the Zeitsch. f. anal. Chemie, 1880, p. 419, and has been very generally accepted for the assaying of pyrites between buyer and seller. Objections made to the accuracy of that process by Jannasch and Richards (Journ. f. prakt. Chem. [2] xxxix. p. 321) have been withdrawn by them (*ibid.* xl. p. 326), and have been completely refuted by experiments made in my laboratory by two independent investigators (Zeitsch. f. angew. Chemie, 1889, p. 473). The process, as it will now be described, may hence be regarded as the most accurate known for the estimation of sulphur in pyrites, where it is desirable *not*

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* Concerning the action of nitric acid on lead sulphate, see my experiments detailed in J. Soc. Chem. Ind. 1887, p. 96.

to include galena and heavy-spar, and it is at the same time very easy and speedy of execution, if the following directions are accurately observed.

About 0·5 grm. of pyrites is heated with about 10 c. c. of a mixture of 3 vols. nitric acid (spec. grav. 1·4) and 1 vol. strong hydrochloric acid, both ascertained to be absolutely free from sulphuric acid. The operation is performed as described above, in such manner that no loss by spurting takes place. The mixture is heated up now and then, till the decomposition is complete, and is then evaporated to dryness in a water-bath. Now add 5 c. c. hydrochloric acid, evaporate once more (no nitrous fumes ought to escape now), add 1 c. c. concentrated hydrochloric acid and 100 c. c. hot water; pass through a small filter and wash with hot water. The insoluble residue may be dried, ignited, and weighed. It may contain, besides silicic acid and silicates, the sulphates of barium, lead, and even calcium, whose sulphur, as being useless, is purposely neglected. (If this residue is not to be estimated, it need not be filtered off, and the next step, the elimination of the iron, may be taken without removing the silica, &c.) The filtrate and washings are saturated with ammonia, avoiding a very large excess of it; the mixture is kept at a moderately warm temperature for about 10 minutes (at the expiration of which time it ought still to smell of ammonia very distinctly, not merely faintly), and the precipitated ferric hydrate is filtered off while the liquid is still hot. For this purpose funnels must be used, made at an angle of exactly 60°, whose tube is not too wide and is *completely* filled by the liquid running through; or else a Piccard's tube (comp. above, p. 65), or a filter-pump is employed. The filtering-paper must be sufficiently dense, but should act rapidly; the filter must be adapted to the funnel so that no air-channel is left between paper and glass. The hot liquid is first decanted from the ferric hydrate, and the latter is then washed onto the filter with boiling water. The washing is continued with hot water in such manner that each time the whole precipitate is thoroughly churned up and no channels are formed in the mass. When acting on these instructions, the whole operation can be performed in from half to one hour, and no trace of sulphuric acid is retained in the precipitate. The total bulk of the filtrate and washings need not exceed 200 or 250 c. c., which saves concentrating the liquid by evaporation. The end of the washing is indicated by the fact that

1 c. c., on adding barium chloride, shows no opalescence even after a few minutes. (It is, however, best in important cases to test the iron precipitate for sulphur by drying it, detaching it as well as possible from the filter, fluxing with pure sodium carbonate, dissolving in hot water, acidulating and adding $BaCl_2$.)

The clear liquid, which now contains all the sulphuric acid combined with ammonia, is acidulated with pure hydrochloric acid in very slight excess, heated to boiling, the burner removed, and 20 c. c. of a 10-per-cent. solution of barium chloride, previously heated, is slowly poured in. This quantity, which suffices in any case for 0·5 gram pyrites, is roughly measured off in a test-tube provided with a mark, and is heated in the same tube. After precipitation, the liquid is left to stand for half an hour, when the precipitate should be completely settled. The clear portion is now decanted, and the washing continued by decantation with boiling water, as mentioned on p. 65, where the mode of igniting the precipitate is also described. The ignited precipitate should be a perfectly white and loose powder, one part of which is equal to 0·13733 sulphur.

The accuracy of this method and its complete accordance (in the case of pure ores) with the fusion method of Fresenius have been proved by Pattinson (Journ. Soc. Chem. Ind. 1890, p. 21), who points out how much more convenient is the former than the latter.

Küster and Thiel (Zsch. anorg. Ch. xix. p. 97) erroneously assume that the ferric hydrate cannot easily be washed by my method so as to remove all sulphate (which is refuted by hundreds of students who have carried out this method in my laboratory, and thousands of chemists elsewhere). They therefore propose to precipitate the barium sulphate without filtering off the ferric hydrate and to remove the latter subsequently by several hours' digestion with hydrochloric acid; or else to prevent the precipitation of ferric salts along with the barium sulphate by the addition of a large quantity of ammonium oxalate. Both methods take much more time than mine, without any gain in accuracy, as I have shown in Zsch. anorg. Ch. ix. p. 454, and again xxi. p. 194. This is confirmed by Herting (Zsch. angew. Ch. 1899, p. 274).

According to Heidenreich (Zsch. anorg. Ch. xx. p. 233) the contamination of barium sulphate by iron salts can be avoided by reducing the ferric sulphate to ferrous sulphate by means of zinc and preventing the access of air and light during the precipitation. Herting and Lehnardt (Chem. Zeit. 1899, No. 75) effect the same purpose much more quickly by employing stannous chloride in lieu of zinc.

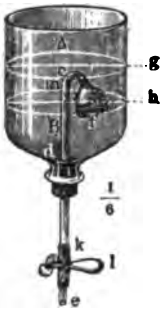
Noaillon (Zsch. angew. Ch. 1897, p. 351) proposes to avoid the filtration of the ferric hydrate by diluting the liquid to a certain mark, filtering, and employing a portion of the filtrate for the precipitation with barium chloride ; but this method introduces more than one error and must be rejected.

Sodium peroxide is proposed for the decomposition of pyrites by Hempel, Höhnel (Arch. Pharm. 1894, p. 222), and Glaser (Chem. Zeit. 1894, p. 1448).

In lieu of the estimation of sulphuric acid by weight, some chemists prefer *titration* by means of a standard solution of barium chloride. This was first proposed by Wildenstein (Zeitsch. f. anal. Chemie, i. p. 432), and afterwards, especially for the analysis of pyrites, by Teschemacher and Smith (Chem. News, xxiv. pp, 61, 66 ; comp. also Glendinning and Edger, *ib.* p. 140). Although this process, notwithstanding some assertions to the contrary, is most certainly no more accurate than the gravimetric process, and in most hands is less so, and is not used by many chemists in important cases, we shall take this opportunity of describing the estimation of sulphates by titration with barium chloride in its simplest form, such as is used at some works in testing black-ash, &c. ; it is also used sometimes in testing pyrites, blende, burnt-ore, &c. for purposes where no great accuracy is required.

The liquid is brought to the boil in a porcelain dish, barium-chloride solution is added from a burette; from time to time a few drops are taken out with a glass tube, passed through a miniature filter onto a glass plate resting on a black background, upon which a number of drops both of dilute sulphuric acid and of barium chloride have been put. If the filtrate still gives a cloudiness with a barium-chloride drop, easily visible on the black ground, the little filter is thrown back into the dish, more barium-chloride solution is added from the burette, another test is made, and so forth. The end is attained when a filtered drop gives an extremely slight cloudiness both with a drop of barium chloride and with one of sulphuric acid. The work is very much expedited by the following contrivance, proposed by Wildenstein and shown in fig. 6. The acidulated solution is poured into a vessel, A, made of a bottle by removing the bottom, or a small tubulated jar, through whose cork passes a bent tube B, provided at the lower end with the pinchcock *l*, at the upper end with a bent-down funnel *f*. The latter (which must be bell-shaped) is closed by two disks of filtering-paper and a piece of linen gauze tied over all; and the liquid must cover the whole tube. This arrangement permits of withdrawing at will small filtered samples of a few drops each, which are run into a test-tube and tried with a drop of barium-chloride solution. It must, of course, not be omitted first to run a few c. c. out of the tube B and back into the jar A before taking the sample for testing; and the contents of the test-tube must be always put back into A, not to waste too much substance. If by accident the point of finishing the reaction has been overstepped, one or more c. c. of titrated sulphuric acid are put in and are afterwards deducted from the result.

Fig. 6.



C. and J. Beringer effect the titration by barium chloride after addition of sodium acetate and acetic acid (Chem. News, lix. p. 41).

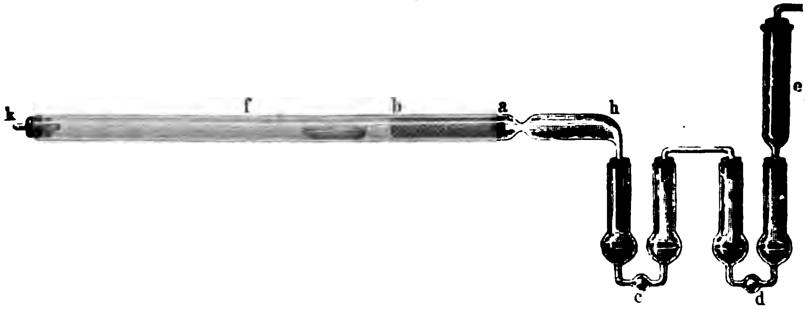
Various other volumetric methods for the estimation of sulphates, by Carl Mohr, Ad. Clemm, Wildenstein (2nd method), Schwarz, and Pappenheim, are described in the treatises of Fresenius and Mohr; but they are more complicated and not more accurate than the direct titration with barium chloride as just described. We, therefore, mention only one method of this kind. This is the method proposed by Wilsing (Chem. Ind. 1886, p. 25), a slight but apparently useful modification of those just mentioned. He precipitates a neutral solution of the sulphate or solution containing such, boiling in a porcelain dish, with a 4-per-cent. barium-chloride solution of known strength; he then adds a few drops of an alcoholic solution of phenolphthalein and a 2-per-cent. solution of sodium carbonate: as soon as the last part of barium chloride has been precipitated as carbonate the colour turns red, so that the soda used is a measure for the sulphate originally present. If the solution to be tested is either acid or alkaline, it must be made neutral by sodium carbonate or hydrochloric acid, phenolphthalein being used as indicator here as well.

L. W. Andrews (Amer. Chem. J. 1889, p. 567, & Chem. Zeit. 1889, Rep. p. 39) proposes the following method for estimating sulphuric acid combined with bases:—The solution is diluted till it contains no more than 2 per cent. SO_3, is almost neutralized and brought to a boiling heat. Now a solution of pure barium chromate in hydrochloric acid is added, and then ammonia, the excess of which is removed by boiling. The solution is filtered while hot and is washed at once. Now a quantity of chromic acid, equivalent to the sulphuric acid originally present, will be in solution; this is estimated by adding potassium iodide and strong hydrochloric acid, and titrating with decinormal thiosulphate-solution (1 c.c. $=12{\cdot}85$ mg. $I=2{\cdot}662$ mg. SO_3). It is claimed that this operation is more quickly performed than the gravimetric process, and is at least as accurate; but both of these assertions are doubtful.

Similar methods are described by Reuter (Chem. Zeit. 1898, p. 357) and Marboutin and Moulinié (Chem. Cbl. 1898, i. p. 218).

Several methods have been proposed for estimating the *available sulphur* of sulphur-ores—that is, that portion of it which passes into the chambers in the shape of SO_2 and SO_3. Thus W. G. Mixter (Amer. Chem. J. ii. p. 396) burns the pyrites in a current of oxygen, and passes the vapours into bromine-water containing some hydrochloric acid and an excess of bromine. A similar process is recommended by Zulkowsky (Wagner's Jahresb. 1881, p. 160), both for testing pyrites and spent oxides of gas-works. The latter is always contaminated with sawdust, tarry matters, and variable quantities of lime, which retains part of the sulphur in burning, whence an estimation of the total sulphur is quite useless for practical purposes. The process takes place in a combustion-tube (fig. 7), 2 feet long, narrowed at *a*, and drawn out at the end into a long tube, not too thin, and bent downwards. Between *a* and *b* there is a layer of platinized asbestos (see below), 8 to 10 inches long, and at a distance of 3 or 4 inches from this a porcelain boat with about 0·4 grm. of spent oxide or pyrites. The end of the tube at *k* is connected with an oxygen gas-holder. The absorption of the vapours takes place in the two 3-bulb tubes *c* and *d* (5½ inches high) and the tube *e*, filled with glass-wool. The absorbing-liquid is made by dissolving 180 grams caustic potash (purified with alcohol from sulphate) in water, adding 100 grams bromine, taking care to keep the mixture cool, and diluting to 1000 c. c. 30 c. c. of this suffice for estimating 0·5 grm. sulphur. The tube *e* ought also to be moistened with it. First heat the portion of the tube between *a* and *b*, passing moist oxygen through it at the same time; then heat the boat from the right to the left; lastly the tube, up to the place *f*. The current of gas must be much stronger than for an organic analysis, lest any sulphur should escape unburnt, but not strong enough to draw off any SO_3 unabsorbed. So long as any dew appears at *h*, it must be driven into the receiver with a Bunsen burner. When this ceases (usually in about an hour), the experiment is finished. The receivers are then taken off, washed out, and the acid remaining in *h* is recovered by aspirating water several times through it. All the liquids are united, supersaturated with hydrochloric acid in order to decompose the potassium hypobromite, heated, concentrated if necessary, and the sulphuric acid is precipitated by barium chloride in the usual manner (or, more conveniently, the receivers

Fig. 7.



are charged with hydrogen peroxides free from sulphuric acid and are retitrated after the end of the operation).

Jannasch (Journ. f. prakt. Ch. [2] xl. p. 237) heats pyrites in a mixture of air or oxygen and nitric-acid vapours; the vapours of SO_2 and SO_3 are absorbed in bromine-water. [It must not be forgotten that in the presence of nitric acid the barium sulphate is never free from nitrate, and that hence all nitric acid must be removed previously. I would, therefore, propose to use in that class of processes hydrogen peroxide as an absorbent, which is very efficient and requires no special precautions; in this case the acids absorbed can be estimated by titration with the standard alkali.]

Graeger (Dingl. Journ. ccxli. p. 53; Fischer's Jahresb. 1881, p. 161) heats pyrites with reduced metallic iron, decomposes the FeS formed by dilute hydrochloric acid, and titrates the H_2S evolved by passing it into a solution of iodine. This method has been again proposed by Treadwell (Berl. Ber. xxiv. p. 1937, and xxiv. p. 2377) and by Eliasberg (Zsch. anal. Ch. 1899, p. 240), but it does not seem to be practically employed.

Expeditious assays of pyrites have been proposed in many ways, but none of them is sufficiently accurate to be employed for estimating the sulphur in fresh pyrites, and some of them are not even accurate enough for testing the sulphur remaining in *burnt-ore* (pyrites cinders).

The so-called *mechanical pyrites assay* of Anthon (Dingl. Journ. clxi. p. 115) is too rough and unreliable even for very simple purposes. (Comp. 1st ed. of this work, i. p. 108.)

In the Freiberg works 1 gram of finely ground pyrites is mixed with 2 grams sodium carbonate and 2 grams saltpetre: the mixture is fluxed in a small iron dish in a red-hot muffle-furnace, dissolved in hot water and filtered into a beaker in which there is hydrochloric acid by saturating the soda in excess. Then the filtrate is brought to boiling, and the sulphuric acid estimated by a standard solution of barium chloride, preferably by Wildenstein's method (*supra*, p. 70). Liebig (Post's Tech. chem. Analyse, 2nd ed. i. p. 677) recommends this method as a quick and easy one, where no great accuracy is required.

In the method of Pelouze (Compt. Rend. liii. p. 685; Ann. de Chim. et de Phys. [3] lxiii. p. 415) the finely powdered pyrites is mixed with chlorate of potash, common salt, and an exactly weighed quantity of sodium carbonate, and ignited, which can be done in an iron spoon. The fluxed mass is dissolved in water, filtered, the residue washed, and the soda not converted into sulphate estimated alkalimetrically. This process continued to be recommended in French treatises till very recently, although its inaccuracy was established and the sources of error partly demonstrated by many chemists, such as Barreswil, Bottomley, Bocheroff, Lunge, and especially Kolb ('Notes sur l'Essai des Pyrites de Fer'). Kolb found the sources of error on the one hand in the formation of sodium silicate, on the other hand in the decomposition of potassium chlorate in the presence of ferric oxide into chlorine, oxygen, and caustic potash. New experiments made in my laboratory by Mr. Rey have equally proved the method to be wrong, even if the "constant error" of 1 to 1½ per cent., admitted by Pelouze, is taken into account. A principal objection is the difficulty of evading the mechanical loss by spurting in the fluxing process.

This fault is avoided in the plan proposed by Kolb (J. pharm. Chim. [4] x. p. 401), which, however, is only intended for testing burnt-ore. Kolb mixes 5 or 10 grams of this with 5 grams pure sodium carbonate and 50 grams cupric oxide, heats about 15 minutes in an iron capsule to a dark-red heat, with stirring, lixiviates the melted mass, and estimates the unconsumed soda volumetrically. The trials made in the author's laboratory showed that there is no spurting, but that the heating must not be prolonged too much, in order to avoid the formation of silicates. The lixiviation of the large bulk of cupric and ferric oxide is tedious, and the method is somewhat costly, as it requires 50 grams of cupric oxide for each test, nor are the results very satisfactory (see below).

A much better method for testing burnt-ore was proposed by J. Watson (J. Soc. Chem. Ind. 1888, p. 305). 2 or 3 grams of pyrites cinders are mixed with 1 or 2 grams of sodium bicarbonate of known titre; the mixture is heated in a nickel, porcelain, or platinum crucible by means of a small Bunsen flame for 5 or 10 minutes, stirred up, heated once more for 15 minutes with a somewhat stronger flame, treated with hot water, filtered and washed. The solution is titrated with hydrochloric acid and methyl-orange; the loss of titre in comparison with the original one is equal to the sulphate formed. The escaping carbonic acid keeps the mass porous; there is no spurting, and the lixiviation of the small bulk of the mixture is easy and expeditious.

Experiments made in my laboratory (Zeits. f. ang. Chem. 1892, p. 447) showed that Watson's method yielded results closely agreeing with those obtained by accurate gravimetrical methods, whilst the method of Pelouze, even with burnt-ore, yielded too low results, and that of Kolb was not more reliable. But it was found that special precautions must be observed in order to yield accurate results. 3·200 grams of the finely ground samples are mixed with 2·000 grams sodium bicarbonate (of known alkalimetrical titre), and heated in a nickel or iron crucible; a platinum crucible easily leads to over-heating. The heating is continued for 10 or 15 minutes with a very small flame, then another 15 minutes with a strong flame, but without fusing the mass. The crucible must be kept covered and the mass must not be stirred; it should in the end be red-hot, and after cooling black and porous. It is boiled in a porcelain dish with water, adding the same volume of neutral solution of sodium chloride. This is an essential improvement, as without this addition some oxide of iron invariably passes through the filter, and makes the following titration by methyl-orange almost impossible. The filtered solution is titrated with standard acid. The difference between the original titre of bicarbonate and that now found shows the sulphur, 1 c. cm. normal acid indicating 0·5 per cent. S. In the presence of a somewhat considerable quantity of zinc this method does not answer.

Magnetic pyrites (*pyrrhotite*), Fe_7S_8, is sometimes present, especially in some kinds of American pyrites. As that ore yields its sulphur very imperfectly in ordinary pyrites-kilns, its estimation may become important. Cone (Journ. Amer. Chem. Soc. xviii. p. 404) effects this by grinding the ore so that all passes through a 60-mesh sieve (not more finely!), spreading the powder on a sheet of glazed paper, applying a magnet to this, removing the mechanically adhering pyrites by gently knocking the magnet and separately brushing off the pyrrhotite after putting on the anchor. This is repeated five or six times, and the sulphur estimated in the separated portions.

Marcasite and pyrites can be distinguished by the easier decomposition of the former when boiling with a solution of ferric salt. This behaviour has been studied in detail by H. N. Stokes

(Bulletin U.S. Geol. Surv. No. 186); but it is of no practical importance for technical analysis.

Estimation of other constituents of Pyrites.—Usually it is sufficient to estimate the sulphur in a pyrites whose nature is otherwise known. If, however, the pyrites is of unknown composition, its value for acid-making can only be estimated by a complete determination of all its constituents according to the rules of mineral-analysis. If it contains, for instance, *calcium carbonate*, this on burning will retain its equivalent of sulphuric acid equal to 0·32 per cent. S for each per cent. $CaCO_3$; if *calcium sulphate* is present from the first, its sulphuric acid has to be deducted from the whole quantity of sulphur found. If *lead* has been found, an equivalent of sulphur must be considered as practically lost; and the same is the case with *zinc*,—because the sulphates of both metals are hardly or not at all decomposed at the temperature of a pyrites-burner. In France half of the S combined with Zn is considered as lost, = 0·245 p. c. S per 1 p. c. Zn (for copper they reckon 0·505 p. c. S per 1 p. c. Cu as lost). Frequently *arsenic* will also have to be sought for; and even *silica* may be of importance—firstly, because in the presence of much silica "explosive" properties of the pyrites must be feared (see p. 55), and secondly, in the case of cupreous pyrites, because silica lessens the value of the cinders. Even *silver* and *gold* are sometimes sought for (comp. Chem. News, xxvi. p. 63, xxxiv. pp. 94, 132, 152, 172); but it cannot be said that the quantities found have any influence on the commercial value of pyrites.

It is not our object here to treat of the estimation of all these substances, nor that of the *copper* which, in the majority of cases, represents a large portion of the value of pyrites *. We make an exception only with *arsenic*, because special methods for estimating this in pyrites have been worked out which are not found in the ordinary text-books.

The process employed at Freiberg is that used by Reich, and is as follows:—Digest about 0·5 gram of finely pulverized pyrites in a porcelain crucible, covered with a watch-glass, with

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* For these substances, see Lunge and Hurter's 'Alkali-Maker's Handbook'; also a very extensive paper by Westmoreland, J. Soc. Chem. Ind. 1886, p. 31, and criticisms on the same, p. 277; and Lunge's Chemisch-Technische Untersuchungsmethoden,' i. p. 250 *et seq.*

concentrated nitric acid at a gentle heat, until the residue assumes a lighter colour and the separated sulphur has turned a pure yellow. After decomposition, heat the crucible on a sand-bath to get rid of the excess of acid, but not to dryness. Add 4 grams of sodium carbonate, dry completely on the sand-bath, add 4 grams of potassium nitrate, and heat the mass until the contents of the crucible have been in quiet fusion for ten minutes. Extract the cooled mass with hot water and filter; the filtrate contains all the arsenic as sodium arseniate. Acidify with a little nitric acid, keep for two hours on a sand-bath to get rid of the carbon dioxide, add a sufficient quantity of a solution of silver nitrate, and neutralize carefully with dilute ammonia. The reddish-brown precipitate of silver arseniate is filtered, washed, dried, taken off the filter as well as possible, the filter is incinerated in a muffle, the precipitate put to it, a sufficient quantity of assay lead is added, and the silver estimated by cupellation. 100 parts of silver correspond to 23·15 of arsenic.

Leroy M. McCay has modified and greatly simplified this method (Chem. News, xlviii. p. 7) by estimating the excess of silver used by Volhard's method. Later on (Amer. Chem. J. viii. no. 2) the same author recommends as preferable another plan, namely dissolving the Ag_3AsO_4 in dilute ammonia, and either estimating the silver by Volhard's volumetric method (precipitation with ammonium thiocyanate), or evaporating, drying, and weighing the total in a thin platinum dish. If the arsenic is to be precipitated as pentasulphide, which is otherwise a tedious operation, McCay recommends (Amer. Chem. J. ix. no. 3, and x. no. 6) to place the solution in a flask with a well-fitting stopper, acidify with HCl, and dilute with freshly boiled water till the flask is nearly full, pass in H_2S to saturation, insert and fasten down the stopper, and place the whole in a water-bath for an hour. At the end of that time all the arsenic will be precipitated as pentasulphide, As_2S_5, containing no free sulphur.

Clark (J. Soc. Chem. Ind. 1887, p. 352) recommends the following method as especially adapted for estimating very small quantities of arsenic in pyrites rich in sulphur:—Mix 3 grams of pyrites in a platinum crucible with four times as much of a mixture of calcined magnesia and sodium hydrate, heat for about 10 minutes over a moderately low Bunsen flame, extract the shrunk mass with boiling water, acidify the solution with hydrochloric acid (which evolves much H_2S), boil for a few minutes, and saturate with H_2S, when all the arsenic will be thrown down as sulphide; wash the precipitate, extract the sulphide of arsenic with ammonia, evaporate the solution to dryness, dissolve in strong nitric acid, and estimate the As as ammonio-arseniate of magnesia, or else by silver solution as above described. Or else the calcined mixture, after neutralizing it with HCl, as above mentioned, is reduced by cuprous chloride, and the liquid is slowly distilled into water, repeating this operation twice with strong HCl, which will cause all the arsenic to pass over as $AsCl_3$, which can be either precipitated by H_2S or titrated by iodine. Clark points out the necessity of carefully testing all the reagents employed for arsenic, of which he had found as much as 0·02 per cent. even in commercial caustic soda.

Nahnsen's process (Chem. Zeit. xi. p. 692; abstr. J. Soc. Chem. Ind. 1887, p. 564) does not offer any special advantage. The process described in detail by H. Fresenius (Zeitsch. f. anal. Chemie, 1888, p. 34) is no doubt very accurate, but lengthy and troublesome.

Blattner and Brasseur (Z. angew. Ch. 1898, p. 262) give exact instructions for estimating arsenic in pyrites, both in the wet and dry methods.

3. ZINC-BLENDE.

This mineral is now the principal zinc-ore. Previously to reducing the zinc, the blende must be roasted in order to convert it into ZnO, and this process was formerly carried out without taking any care to deal with the enormous quantities of SO_2 formed. Sanitary legislation at last interfered with this procedure, which of course laid waste all the country round the zinc-works, and compelled measures for dealing with the noxious gases. Part of this is used for the production of liquid sulphur dioxide (comp. Chap. IV.); most of it, however, serves for the manufacture of sulphuric acid, so that blende has now become one of the more important raw materials for this purpose. The historical development of this industry will be related in Chap. IV.

Blende occurs in large quantities for instance in Silesia, Westphalia, Rhineland, Saxony, Austria, Belgium, Wales, the Isle of Man, Spain, Italy, France, the United States, in nearly all of which localities it is utilized for the manufacture of sulphuric acid.

Pure blende, ZnS, contains 32·9 per cent. S, and 67·1 per cent. Zn. The commercial ore is, of course, always impure. We quote the following analyses, by Minor (Chem. Zeit. 1889, p. 1602), of Rhenish blende :—

S	30·24	27·94	22·11	21·05
Zn as ZnS	22·73	27·17	34·46	31·16
Zn in other combination	5·03	4·75	5·83	6·65
Fe	15·98	13·12	2·06	2·33
Gangue (by diff.)	21·02	27·02	35·54	38·84

Drasche analyzed a blende from Carinthia: ZnS 68·41 per cent., PbS 4·55 ; FeS_2 2·05 ; $ZnCO_3$ 2·40 ; $CaCO_3$ 8·93 ; $MgCO_3$ 10·62 ; Al_2O_3 0·63 ; gangue (principally quartz) 2·32 per cent.

Pennsylvanian blende, according to F. A. Genth :—Sulphur 32·69 to 33·06 per cent., Zinc 66·47, Iron 0·38, Cobalt 0·34.

Jurisch (Schwefelsäurefabrikation, p. 61) quotes analyses of various descriptions of blende, burnt by the Chemische Fabrik, Rhenania, with sulphur contents varying from 18·40 to 32·20, and zinc from 14·90 to 50·22 per cent.

Haenisch and Schroeder (Chem. Ind. 1884, p. 118) quote the contents of Silesian blende=23 to 37 per cent. S, also an inferior blende=8 to 21 per cent. S.

Blende frequently contains cadmium and mercury. The latter occurs in Rhenish blende only =0·02 per cent., but in Spanish (Aviles in Asturia) =0·135 per cent.

According to direct information from the Rhenania Chemical Works at Stolberg, the sulphur contents in the blende roasted there ranges between 20 and 30 per cent.; on the average 25 to 28 per cent. Iron does not do any harm, but lime retains its equivalent of S as $CaSO_4$. Lead affects the duration of the roasting-floors ; it is partially volatilized with a little silver, and reappears in the flue-dust, the towers, and chambers. Mercury and fluorine are also volatilized and act very injuriously on the platinum vessels used for concentration. Recently the sulphuric acid factories refuse blende containing fluorides. Arsenic generally occurs in blende in such extremely slight quantities that the acid made from it may be considered as technically pure.

The production of blende in Prussia in 1890 amounted to

362,464 tons; Belgium in 1889 to 12,376 tons; France and Algiers in 1887 to 13,800 tons; Spain in 1885 to 2,488 tons.

Analyses of Zinc-blende.—The sulphur is estimated by the wet method as described p. 62. In the *cinders* from blende the same method must be employed since the dry methods, *e. g.* Watson-Lunge's (p. 75), give quite wrong results. Details respecting this and the other constituents of zinc-blende are found in Lunge and Hurter's 'Alkali-Maker's Handbook' and Lunge's 'Chemisch-technische Untersuchungsmethoden.'

4. OTHER METALLIC SULPHIDES.

Pyrites proper has hardly any other application than that for sulphuric-acid making, and it is obtained almost exclusively for this purpose. In the case of cupreous pyrites the sulphur constitutes only a portion, but a very considerable one, of its value. The working of poor copper-ores would not pay, apart from the noxious effect of the gas produced in calcining the ore, unless the price of the ore were very moderate; and this is only possible by the acid-makers paying on their part for the ore, which they can well afford, as most kinds of cupreous pyrites behave very well in the burners, and yield quite as much acid in proportion to their percentage of copper as the non-cupreous ores. The case of zinc-blende is now similar to that of cupreous pyrites.

The case is different with most other sulphuretted ores occurring in smelting-operations, such as *galena,* the many *mixed ores* containing blende and galena, besides iron- and copper-pyrites, the richer *copper-pyrites* themselves, and, lastly, the intermediate products, *"coarse metal," "matte,"* &c. These, for their metallurgical utilization, equally require a calcination evolving sulphur dioxide; but the matter is very different here from what it is with a good pyrites, whether it be pure iron-pyrites or containing a few per cent. of copper. On the whole, all those ores and metallurgical products are much poorer in sulphur than ordinary good pyrites; and for this reason they are less easily calcined in such a manner as to allow of utilizing the gas, because the evolution of heat by the combustion of their own sulphur is not sufficient to maintain the process energetically. An external stimulus was required before smelting-works would seriously attempt to utilize the sulphur dioxide contained in the gas from calcining the ores; and this proved to be the damage and nuisance caused by the ***noxious vapours*** all round the works. The claims for damages, the law-suits, and the measures taken by the authorities at last made it impossible in many places for the works to go on in the old way; and although it appeared at first as if the sulphurous acid could not be condensed at all in this case, or only at a loss, practice has now succeeded in fulfilling the task in most (but not in all) cases, principally by the construction of improved burners, which will be described in the fourth Chapter. It would undoubtedly be too much to say that the task had been solved in all its parts; the success has mostly been only partial. In many cases where an ore could not possibly have been calcined so as to utilize the gas, mixing of it with others has been resorted to. Thus the Halsbrücke works, near Freiberg, roast galena and blende along with pyrites ; and in 1870 they made 8000 tons of sulphuric acid from the gas.

In reference to the sulphur dioxide escaping as noxious vapour, Leplay (comp. Percy, 'Metallurgy,' 1862, i. p. 337) mentions that in South Wales annually 46,000 tons of sulphur escaped into the air as sulphur dioxide, along with arsenic, fluorine, lead, and zinc compounds, in spite of the condensing-chambers. In fact the country round Swansea was stripped of all vegetation. At Freiberg the works in 1864 paid upwards of £2750 damages on account of their vapours, in 1870, after better condensation had been effected, only £239. It should not be forgotten that sulphur dioxide occurs in very large quantity, although in a much more dilute state, in all coal-smoke, and consequently in the atmosphere and the rain-water of all large towns, and that the most perfect "smoke-combustion" cannot do away with this. Much more injurious than the vapours escaping through high chimneys, which are soon diluted with air, is the smoke from brick-works, coke-ovens, and other fires which emit their smoke at a low height above the ground. Mr. Fletcher has calculated that at St. Helens the acids escaping amounted :

From fire-gases	to 800	tons	per week.
„ copper-works......	„ 380	„	„
„ glass-works.........	„ 180	„	„
„ alkali-works	„ 25	„	„

Similar calculations have been made by Mr. Hasenclever (Chem. Industrie, 1879, p. 225), who has given strong proof of the damage done by coal-smoke alone.

According to the 28th Alkali Report (for the year 1891), p. 19, the quantity of acid gas which escapes into the air at St. Helens, calculating HCl as its equivalent of sulphur acids, is as follows :—

	Tons sulphur per annum.	
From Copper and Lead smelting works	11,480	19,313
„ Glass-works	7,500	
„ Polishing-powder works	333	
„ Coal burnt (1½ per cent. of 1,040,000) ...	...	15,600
„ Chance-Claus process	...	620
„ Sulphuric-acid chambers	173	575
„ Alkali-works	402	
Total		36,108

This is the equivalent of 72,216 tons SO_2 or 110,586 H_2SO_4, of which the alkali-works contribute only 1½ per cent. Since all this is given off from an area of about 3 square miles, each square mile at St. Helens receives the equivalent of 12,036 tons of sulphur, against 11 tons in summer or 44 tons in winter on a square mile in London.

In Chapter IV. we shall deal with the various attempts at utilizing, or at least rendering innocuous, the acid gases given out in calcining ores, and we shall here enumerate only the various classes of ores or waste substances coming under the head of causing "noxious vapours," such as might serve for the manufacture of sulphuric acid (apart from zinc-blende, comp. p. 79).

Copper-pyrites and mixtures of this with blende, galena, &c. are roasted in several places in kilns so as to utilize the SO_2 in acid-chambers—at Chessy near Lyons, at Oker in the Harz, at Manzfield, at Swansea. At the Altenau silver-works near Clausthal, in 1872, 228 tons of vitriol of 106° Tw. were made from copper-pyrites (and 314 tons from lead-matte, Wagner's 'Jahresb.' 1874, p. 276). At Freiberg the Mulden and Halsbrücke works proceed in the same way; but they only utilize ores and products pretty rich in sulphur for vitriol-making.

The following particulars respecting the materials burned at the Government works at Oker in 1901 have been communicated to me from an official source. The ores are :—

	Lumps.		Total.
	Tons.	Tons.	Tons.
Copper-ores No. 1	1,205	895	2,100
„ 2	4,095	88	4,183
„ 3	1,417	73	1,490
Mixed ores	7,916	3,770	11,686
Pyritic lead-ore	805	64	869
Copper-matte	6,288	...	6,288
Lead-matte	3,377	...	3,377
"Spurstein" (regulus)	...	1,620	1,620
	25,103	6,510	31,613

Composition of these materials :—

	Copper-ore.			Mixed ore.	Pyritic lead-ore.	Copper-matte.	Lead-matte.	Regulus.
	1.	2.	3.					
Cu	17·70	9·70	4·75	4·60	1·05	30·47	18·20	64·38
Fe	23·00	30·40	33·50	12·40	24·50	24·40	21·70	8·93
Zn	9·50	5·80	4·90	21·50	15·50	8·75	15·00	1·34
Pb	3·70	2·40	1·75	10·05	6·75	5·80	7·10	2·95
S	32·00	36·00	40·50	24·00	34·00	18·70	17·00	20·70

The production of acid at Oker is per annum 21,000 tons. 50° B., in 5 sets of chambers of 19,656 cub. mtrs. capacity, *i. e.* 1068·38 kg. acid of 5° B., per 1 cb. m. chamber-space. The kiln-gases have 4 to 5 per cent. SO_2.

Traces of Hg, Tl, Cd, and Se have been found both in the ores and in the products obtained therefrom.

Apart from pure pyrites, the "ordinary ores" are best adapted for vitriol-making, because they contain their sulphur mostly as FeS_2; the "mixed ores" are less favourable, on account of their galena, and the rich copper-ores on account of their large percentage of copper. Of the lead-ores only those amply permeated by pyrites are fit for vitriol-making. The sulphur in the ores worked at Oker varies from 20 to 40 per cent.; on an average it is 30 per cent.; but it must be noticed that the sulphur of the galena is altogether unavailable for vitriol-making. The case is not much better when copper-pyrites predominates, because this furnishes too poor a gas, and, moreover, decrepitates and falls to powder in roasting. If no more than 35 per cent. of copper-pyrites is mixed with iron-pyrites, it does no harm. Blende behaves in a similar way, but rather more favourably; ores containing 35 per cent. blende along with 25 per cent. pyrites yield gas quite adapted for vitriol-making.

The first sulphuric-acid works at Oker were erected in 1841; there is now one of the largest acid works in Germany, viz. 14 sets of chambers with a capacity of 800,000 cubic feet.

Galena is probably nowhere worked in such a way as to extract its sulphur in the shape of sulphuric acid. The purest galena contains only 13·4 per cent. of sulphur; it is transformed into lead sulphate on roasting, and only in the strongest white heat gives off a portion of its sulphur as SO_2; moreover the metallurgical processes to which it is subject are of such a nature that only poor gas can be produced from it. This subject has been discussed by Bode in his 'Beiträge zur Theorie und Praxis der Schwefelsäurefabrikation,' 1872, pp. 32 & 63; his conclusion is that even mixtures of galena and pyrites cannot be roasted in kilns for vitriol-making if they contain more than 18 to 20 per cent. of galena.

"*Coarse metal*" of copper-smelting is roasted for vitriol at Mansfeld. A product containing 34 per cent. Cu, 28 per cent. Fe, and 28 per cent. S, according to Bode, yields gas with 5½ per cent. by volume of SO_2, and at a sufficiently high temperature to work with the Glover tower. In most cases, up to the present, coarse metal cannot be roasted so as to utilize the SO_2.

Lead-matte is used for vitriol-making—for instance, at Freiberg and in the Lower Harz; it is there roasted in large kilns of 12½ tons capacity. The matte loses half its sulphur, and yields gas with 4 to 6 per cent. of SO_2; the temperature, according to Bode, is high enough for the Glover tower. In the Upper Harz the utilization of its sulphur in metallurgy has in general not been found practicable.

5. BY-PRODUCTS OF OTHER MANUFACTURES.

(*Spent oxide of gas-works, soda-waste, ammonia-works, &c.*)

The spent oxides from the purification of *gas* by hydrated ferric oxide are in many places used for vitriol-making. This sulphur originally also comes from pyrites, viz. from that contained in the coal, which appears in the gas mostly as sulphuretted hydrogen. Most works remove it from the gas by a mixture of hydrated iron oxide and sawdust. In this case sulphide of iron and sulphur are formed, according to the equation

$$2Fe(OH)_3 + 3H_2S = 2FeS + S + 6H_2O;$$

and when the mass, having become inactive, is exposed to the air, it again passes over into ferric hydroxide, more sulphur being precipitated, thus:

$$2FeS + O_3 + 3H_2O = 2Fe(OH)_3 + S_2.$$

The hydroxide thus reproduced and mixed with sulphur is again used in the purifiers, and is regenerated about 30 or 40 times before the sulphur has accumulated therein to such an extent that the mixture does not work any longer; it is then replaced by fresh oxide, and the spent ore is passed over to vitriol-makers.

Phipson states the composition of such a mass to be:—

Water	14	per cent.
Sulphur	60	„
Organic substance insoluble in alcohol.	3	„
Organic substance soluble in alcohol (calcium ferrocyanide and sulphocyanide, ammonium sulphocyanide, ammonium chloride, hydrocarbons).	1·5	„
Clay and sand	8	„
Calcium carbonate, ferric oxide, &c.	13·5	„

If the oxide contains considerable quantities of cyanides, it may cause great trouble in the manufacture of sulphuric acid (31st Alkali Report, p. 89).

Hot water extracts the ferrocyanides and sulphocyanides, along with ammonium chloride; the solution can be evaporated to dryness, and the residue separated by alcohol into insoluble calcium ferrocyanide and soluble sulphocyanide and chloride.

According to the analyses of Davis ('Chemical News,' xxix. 1874, p. 30), three samples of spent oxides contained:—

	I.	II.	III.
Sulphur	64·376	62·358	67·956
Ferric hydroxide	14·421	17·112	15·335
Insoluble	11·052	5·099	8·304
Moisture	2·079	5·387	3·900
Lime (as CaS)	2·399	......	......
Sawdust	2·470	1·776	1·002
Calcium carbonate	......	5·135	3·006
Ammonium sulphocyanide	2·662	1·324	1·102
Ammonium chloride Ammonium cyanide	0·605	......	......
Ammonium ferrocyanide	......	1·663	......
Prussian blue	trace	0·366	trace
	100·064	100·220	100·605

These samples seem to have been taken from precipitated iron hydroxide, to judge from further analyses by Davis (Chem. News, xxxvi. p. 189), in which also tarry substances are taken into account.

Residues proceeding from

	Precipitated $Fe(OH)_3$.	Bog-iron-ore.	Copperas.	Bad oxides.
Ferric hydroxide	17·74–19·36	15·96–26·42	5·04– 6·84	8·72–20·40
Sawdust	1·98– 4·72	1·14– 3·72	1·04– 3·24	2·16– 9·76
Calcium carbonate	0· – 1·04	0· – 1·73	0·	0· –10·36
Ammonium sulphocyanide	1·99– 2·74	0·94– 1·93	1·98– 3·41	1·18– 4·72
Ammonium ferrocyanide	trace	trace– 0·21	0·27– 0·64	trace– 0·44
Tarry matters	0·72– 1·22	0·92– 1·14	0·72– 1·18	0·55– 1·04
Sulphur	62·44–67·18	48·76–57·44	48·76–55·74	32·42–42·16
Insoluble in dilute HCl	3·66– 5·47	9·74–11·42	7·82–12·68	12·12–20·71
Prussian blue	....	trace– 0·17	trace– 1·74	trace– 0·64
Calcium sulphate	....	....	trace– 1·43	0· – 3·23
Ammonium sulphate	....	....	12·78–16·72	0· – 1·14
Moisture (by difference)	4·72– 5·76	7·22–10·82	7·98– 9·22	7·49–33·41

From these analyses it can be seen, first, that it is decidedly best to extract the mass at first with water, in order to remove the ammonia compounds, which are in themselves valuable, and which, if they get into the chambers, destroy a good deal of nitre (their value is certainly greatly lessened by the sulphocyanide); secondly, that sometimes a considerable quantity of calcium carbonate is present, which may get into it at the gas-works by lime being added, on purpose or by mistake, and which, of course, retains an equivalent quantity of sulphur in the shape of gypsum. In fact a sample of the residue left after burning contained

Insoluble	33·386
Ferric oxide	52·399
Calcium sulphate	13·315
Sulphur	0·200

These impurities (which cause a loss by retaining sulphuric acid) and the sulphates present from the first (which are not available) must be allowed for in analyzing. This, according to Davis, was formerly done by extracting the sulphur by means of carbon bisulphide, evaporating the solution, and weighing off the sulphur; but as the presence of tarry matters causes an error, Davis now makes the analysis by burning the sulphur in a current of air in a combustion-tube of Bohemian glass, conducting the SO_2 formed into an absorbing-apparatus filled with iodine solution, and retitrating the unaffected iodine by a solution of sodium thiosulphate (Chem. News, xxxvi. p. 190; comp. also Zulkowsky's process, p. 72).

The burning of this gas-sulphur is usually done in shelf-furnaces similar to those used for pyrites-smalls. They will be described in detail in the fourth Chapter. Already in 1861, at Barking Creek, on the Thames, 2180 tons of this material were used; but much larger quantities might have been got, since, according to A. W. Hofmann ('Report,' 1862, p. 15), even at that time at least 10,000 tons of sulphur were contained in the London gas. Much of the acid made from spent oxide is sold as "brimstone acid."

In France also, at that time, the sulphur from gas-works was used on a large scale. The factory at Aubervilliers, belonging to the Society of St.-Gobain, used no other; Messrs. Seybel and Co. at Liesing, near Vienna, and Kunheim and Co. at Berlin (Wagner's Jahresb. 1864, p. 153; Hasenclever, *l. c.* p. 167) do the same.

The rational treatment of spent oxides for the purpose of obtaining ammonium salts, ferrocyanides, and sulphocyanides is described in Lunge's 'Coal-Tar and Ammonia,' 3rd edition, p. 716.

The sulphur contained in *alkali-waste*, in the shape of calcium sulphide, has been frequently proposed for the manufacture of sulphuric acid, nearly always after having been first converted into *sulphuretted hydrogen*. The only successful process in this line (the Chance process of treating alkali-waste) belongs to the domain of alkali-manufacture, and cannot be treated in this volume. Only the contrivances for burning the hydrogen sulphide will be described in the fourth Chapter.

Bornträger (G. P. 15,757) proposes decomposing the yellow liquors from alkali-waste by means of ferric oxide (ground damp pyrites cinders), to filter the sulphur and ferric sulphide which is thus precipitated, and burn it after drying in ordinary shelf-burners. [Oxide of iron in this state is a very inferior reagent for removing the sulphur from yellow liquors and the like.]

An anonymous inventor has proposed to absorb the sulphuretted hydrogen in hydrated ferric oxide suspended in water, filter, press the residue, dry it, and burn it on shelf-burners. Wyss (Bull. Soc. ind. Mulh. 1890, p. 281) has shown that this process is neither novel nor in any way promising of success.

The sulphuretted hydrogen given off in the manufacture of sulphate of ammonia (comp. Lunge's 'Coal-Tar and Ammonia,' 3rd ed. p. 857) is sometimes used for the manufacture of sulphuric acid. Here the H_2S is not merely diluted with a large quantity of inert gases, but is also of very unequal concentration, which formerly rendered the manufacture of sulphuric acid from this source an unprofitable process. The same can be said of most other cases in which H_2S is given off as a by-product.

The utilization of the H_2S from sulphate-of-ammonia works for the manufacture of sulphuric acid has, however, been greatly improved and is now no longer a rare exception, but is practised in a good many English works. If the gas is properly introduced into the burner (comp. Chapter IV.), the consumption of nitre is not excessive, and it is even possible to increase the heat by this means, if the spent oxides should not suffice for this purpose. The action of the large quantity of carbon dioxide accompanying the H_2S in the case of sulphate-of-ammonia works would seem to consist only in requiring a certain amount of chamber-space, contrary to the opinion reported in Chapter VIII.

Sulphur dioxide, formed in many manufacturing operations as a disagreeable by-product, apart from those already described, is sometimes proposed to be converted directly or indirectly into sulphuric acid. The special cases in which this has been attempted will be treated in the next Chapter.

6. NITRATE OF SODA, NO_3Na (commonly called "Mere").

$\frac{1}{2}(Na_2O)$	= 31·05	36·49 per cent.
$\frac{1}{2}(N_2O_5)$	= 54·04	63·51 „
	85·09	100·00

Hardness 1·5 to 2; spec. grav. 2·09 to 2·39. In the pure state, and in large crystals, it is colourless, transparent, and brilliant as glass; in small crystals it is white and opaque. The crystals are rhombohedra with angles of 106° 30′ and 73° 30′. It has a cooling, bitter taste. Heated to a certain temperature it melts; at a red-heat it is decomposed into sodium nitrite and oxygen gas. The fusing-point is 316°–319° C. (Carnelley, J. Chem. Soc. 1878, ii. p. 277). Mixed with coal, deflagrates on heating. It attracts moisture from the air (especially if not quite free from chlorides), and readily dissolves in water, with a considerable lowering of the temperature.

1 part of sodium nitrate, according to Marx, requires for solution 1·58 part of water at −6°, 1·25 at 0°, 0·46 at +119° C. According to Kopp, 1 part of sodium nitrate at 18°·5 C. requires 1·14 of water, or 100 parts of water dissolve 87·72 parts of the salt. In the presence of sodium chloride its solubility is considerably less.

Specific Gravity of the Solutions of Sodium Nitrate at 20° C.

Parts of salt in 100 water.	Specific gravity.	Parts of salt in 100 water.	Specific gravity.
1	1·0065	21	1·1498
2	1·0131	22	1·1578
3	1·0197	23	1·1659
4	1·0264	24	1·1740
5	1·0332	25	1·1822
6	1·0399	26	1·1904
7	1·0468	27	1·1987
8	1·0537	28	1·2070
9	1·0606	29	1·2154
10	1·0676	30	1·2239
11	1·0746	31	1·2325
12	1·0817	32	1·2412
13	1·0889	33	1·2500
14	1·0962	34	1·2589
15	1·1035	35	1·2679
16	1·1109	36	1·2770
17	1·1184	37	1·2863
18	1·1260	38	1·2958
19	1·1338	39	1·3055
20	1·1418	40	1·3155

Parts of salt in 100 water.	Specific gravity.	Parts of salt in 100 water.	Specific gravity
41	1·3255	46	1·3761
42	1·3355	47	1·3864
43	1·3456	48	1·3968
44	1·3557	49	1·4074
45	1·3659	50	1·4180

Nitrate of soda occurs in many places in small quantities; but the only large beds which supply the world with this article are situated in a region of the west coast of South America, formerly belonging to Peru and now to Chili. This occurrence, and the industry founded thereon, have been described in various communications by Langbein (Wagner's Jahresb. 1871, p. 300; 1872, p. 290; 1879, p. 390); also by W. E. Billinghurst, of whose book (written in Spanish) Darapsky gives an extract in the 'Chem. Zeit.' xi. p. 752 (J. Soc. Chem. Ind. 1887, p. 545). Comp. also Buchanan (*ibid.* 1893, p. 128) and Behrend (Zschr. deutsch. Ingen. 1899, p. 1199; Fischer's Jahresb. 1899, p. 406).

The nitre-beds are principally situated in the province ot Tarapacá, between 68° 15′ and 78° 18′ longitude, and 19° 12′ and 21° 18′ 30″ latitude; they also occur somewhat south, especially near Antofagasta and Taltal. They were discovered in 1821 by Mariano de Rivero, and have been worked since 1830. The nitre zone is situated at an altitude of 3600 feet above the sea-level.

The total area of the nitre-bearing strata is estimated by Billinghurst at 21,212 estacas (about 150,000 acres), and the yield obtainable therefrom = 1980 millions of Spanish cwts. The nitre-bearing rock, called *caliche,* is found in layers of from 10 inches to 5 feet in depth, which rarely crop out at the surface. The overlying rock, called *costra,* is 18 inches to 7 feet thick, and consists principally of a hard conglomerate of sand, felspar, phosphates, and other minerals.

The composition of the caliche varies; it contains from 48 to 75 per cent. of sodium nitrate, 20 to 43 per cent. of sodium chloride, and varying quantities of sodium sulphate, calcium sulphate, potassium nitrate, potassium iodate, magnesium chloride, also insoluble earthy portions and organic substance (guano). It is first broken by a stone-breaking machine, and then put into the dissolvers. These are partly open square tanks, preferably, however, closed egg-shaped boilers with two manholes—one on the top for filling in the caliche, another at the bottom for emptying the residue. The mass rests on a perforated bottom. The boilers are filled entirely with the broken rock, and half with mother-liquor, and were formerly always heated by direct steam injected below the false bottom. After 1¼ to 2½ hours the liquid, then sufficiently saturated with nitre, is run into settlers; from these it flows, after several hours, into a second settler, where, by half an hour's rest, it allows some still-suspended common salt to subside, and then runs into shallow coolers. The residue from the dissolvers, which still contains 15 to 35 per cent. of sodium nitrate, is either emptied at once or boiled again with fresh water. The crystals, separated in the coolers after draining off the mother-liquors, are spread in layers of 12 to 18 inches thickness on a large surface exposed to draught, and dried with frequent stirring. The total cost of sodium nitrate, up to its reaching European ports, in 1871, amounted to £8 18*s*. per ton, which left a good margin for profit at the average price of £12 (it has reached £16 and more). At present both the producing and selling prices are much lower.

The above-described system of dissolving by open steam was afterwards abandoned for closed steam-coils or similarly-acting apparatus; at the same time air heated to 120°–150° C. is forced through the liquid by means of injectors, in order to hasten the evaporation. This produces both stronger and purer liquors, the quantity of sodium chloride being the same in the stronger as in the weaker liquor.

The composition of the crude nitre-earth is shown by the following analyses :—

	Caliche.				Costra.
	a.	*b.*	*c.*	*d.*	*e.*
Sodium nitrate	70·62	60·97	51·50	49·05	18·60
Sodium iodate	1·90	0·73	...	...	...
Sodium iodide	...	...	traces	traces	...
Sodium chloride	22·39	16·85	22·08	29·95	33·80
Sodium sulphate	1·80	4·56	8·99	9·02	16·64
Potassium chloride	...	...	8·55	4·57	2·44
Magnesium chloride	...	...	0·43	1·25	1·62
Magnesium sulphate	0·51	5·88	...	...	...
Calcium sulphate	0·87	1·31	...	...	...
Calcium carbonate	...	...	0·12	0·15	0·09
Silica and ferric oxide	...	...	0·90	2·80	3·00
Insoluble	0·92	4·06	6·00	3·18	20·10
Moisture	0·99	5·64	...	...	...
	100·00	100·00			

The analyses *a* and *b* (*a* white, *b* brown caliche) are by Machattie (Chem. News, xxxi. p. 263). They are somewhat suspicious, both on account of the total absence of potassium salts and of the extremely improbably high percentage of sodium iodate. This is all the more noticeable as Machattie at the same time states the average percentage of iodine in five samples of *mother-liquor* to be =0·56, equal to 0·873 per cent. of sodium iodate, which may be nearer the truth. The analyses *c*, *d*, and *e* are by V. L'Olivier (Compt. Rend., 26th October, 1875).

The iodine contained in the mother-liquors is now recovered to a great extent, and forms one of the principal sources of this article.

Another bed of nitrate of soda has been found in the South-American State of Colombia (Journ. Soc. Chem. Ind. 1894, p. 1001). It is about 100 kilometres distant from San Juan de la Cienaga, and had been proved up to that time for a surface of 75 square kilometres. It has a thickness of from 30 centimetres to 3 metres, and averages 11 to 12 per cent. $NaNO_3$, together with calcium carbonate, calcium sulphate, and silicates. The recoverable nitre is estimated to exceed 7 million tons, but none of it is as yet in the trade. Another bed has been discovered in Texas ; this is stated to contain 98 per cent. pure nitrate (Chem. Ind. 1902, p. 265).

A deposit of *potassium nitrate* has been found near Cochabamba, in Bolivia (Sacc, Compt. Rend. xcix. p. 84). This deposit, reported to be enormous, but not yet worked, consists of 60·70 per cent. potassium nitrate, 30·70 borax, a little salt and water, 8·60 organic substances. On dissolving the saline mixture in hot water and cooling, pure potassium nitrate crystallizes out.

The consumption of nitrate of soda during the years 1898 to 1901 has been as follows :—

	1898. Tons.	1899. Tons.	1900. Tons.	1901. Tons.
Continent of Europe (chiefly Germany)	904,500	981,000	1,026,000	1,036,000
United Kingdom	132,500	121,000	126,000	118,000
United States	125,000	133,000	170,000	192,000
Other countries	16,000	25,000	28,000	18,000
Total ...	1,178,000	1,260,000	1,350,000	1,364,000
Price on 31st Dec., per cwt.	...	7*s*. 9*d*.	8*s*. 6*d*.	9*s*.

(Statistics of previous years are given in the first two editions of this book, pp. 80 and 81.)

When *emptying nitrate of soda from the bags* a certain quantity of the salt, which is always damp, remains adhering to them; this not only causes loss, but renders them useless, and even produces a danger of fire. It is therefore well to lixiviate the bags with hot water and to dry them. The solution is evaporated to a small bulk and crystallized. The mother-liquor from this operation is always very rich in chlorides, which seems to show that the deliquescence of sodium nitrate is not a property of the pure salt, but is owing to the magnesium and calcium chloride contained in it, since the dampest salt will adhere to the bags. The washed and dried bags should not be stored in quantity, as they are still very inflammable.

Composition of Commercial Nitrate of Soda.—R. Wagner (Jahresb. 1869, p. 248) found in commercial nitrate of soda :—

Sodium nitrate	94·03
„ nitrite	0·31
„ chloride	1·52
Potassium chloride	0·64
Sodium sulphate	0·92
„ iodate	0·29
Magnesium chloride	0·93
Boric acid	traces
Moisture	1·36
	100·00

The nitrate of soda imported into England, as used by vitriol-makers, is much purer than the above sample. The English sellers mostly guarantee a maximum of 5 per cent. "refraction" (that is, the total percentage of all foreign constituents, inclusive of water), frequently, however, 4 or even 3½ per cent. refraction. English vitriol-makers would, indeed, altogether refuse nitrate containing upwards of 3 per cent. of chlorides, like that analyzed by Wagner, 1 per cent. being the maximum allowed. The muriatic acid generated from them, of course, gives, with nitric acid, free chlorine and its compounds with nitrogen oxides, and causes a loss of the latter. The average composition of nitrate for chemical works is

96 sodium nitrate (including nitrate, iodate, &c.),
0·5 chlorides (calculated as NaCl),
0·75 sulphates (calculated as $NaSO_4$),
2·75 moisture.

Gilbert (Zsch. f. angew. Chem. 1893, p. 495) pointed out that the Chilian nitre always contains, and always has contained, some *potassium nitrate*. He states that the percentage of KNO_3 rarely exceeds 5 per cent., and the deficiency of nitrogen caused thereby is more than compensated by the value of the potassium for agricultural purposes. The old method of testing for "refraction" is obstinately adhered to by the producers, and is preferred by Gilbert to the direct guarantee of 15·57 per cent. nitrogen demanded by the agricultural control-stations. Jones (*loc. cit.* p. 698) mentions that he had met with nitre containing much more potash; but this nitre, which is recovered from the bilge-water of the carrying vessels, occurs only quite exceptionally (comp. below). Most suphuric-acid manufacturers do not share Gilbert's opinion: see below.

An impurity formerly entirely overlooked in commercial nitrate of soda consists in *perchlorate* and perhaps also *chlorate* of sodium.

Beckurts (Arch. d. Pharm. ccxxiv. p. 323; Fischer's Jahresb. 1886, p. 305) found in all descriptions of commercial nitre small quantities of chlorates and perchlorates, and this has been confirmed from all sides. A large number of methods have been devised for estimating the perchlorate (comp. Lunge's Chem.-techn. Untersuchungsmethoden, i. p. 283 *et seq.*), all of which are practically founded upon converting the perchlorate into chloride, preferably by fusing the nitrate with lime or sodium carbonate and manganese peroxide, estimating the chloride in the ordinary way, and deducting the chloride previously existing in the nitrate.

In order to manufacture nitrate of soda free from perchlorate, which does not occur in the first crystallization, but accumulates in the mother-liquors, and after using these three or four times over contaminates the nitrate crystals up to 1 per cent., H. Foelsch & Co. (G. P. 125,206) cools down the impure mother-liquors to 0° C., 1 cub. metre of which then furnishes 160 kil. of a mixture of salts, containing 150 $NaNO_3$ and $NaClO_4$. The new mother-liquor, when employed for redissolving crude nitre, at first furnishes nitrate free from perchlorate.

Analysis of Nitrate of Soda.

In the laboratories working for the importers of nitrate of soda the value of nitrate is mostly only estimated indirectly, viz. the "refraction." 10 grams are well dried in a porcelain capsule, weighed again, dissolved, the residue (if any) is estimated, the liquid dissolved to a certain volume, and in separate portions of the liquid the chloride and sulphate are estimated in the usual way. The sum total of moisture, insoluble residue, sodium chloride, and sodium sulphate is called the "refraction," and it is assumed that the remainder is real sodium nitrate. This may, however, lead to very erroneous results, where, for instance, the nitre contains some potassium nitrate. A case in point has been described by me in 'Chem. Ind.' 1883, p. 369, where an error amounting to 2 per cent. was caused in this way. Perchlorate causes also errors; and altogether it stands to reason that the consumer of nitrate receives justice only by a real determination of the nitric acid contained in (or, more properly speaking, to be evolved from) a sample of nitrate. On the other hand, the interests of the importers and dealers in nitrate are quite the opposite. According to Fischer's Jahresb. 1899, p. 407, the Hamburg importers insist upon the "indirect" (*i. e.* altogether deceptive) analysis, and want the perchlorate to be counted as nitrate.

The direct analysis, *i. e.* the estimation of the $NaNO_3$ (or its equivalent of KNO_3), can be carried out in many ways, a complete enumeration of which is found in my 'Chemisch-technische Untersuchungsmethoden,' i. p. 273 *et seq.* Among these, those mostly used are the Schloesing-Grandeau and the Ulsch methods (comp. below, in the section on Nitric Acid), but at sulphuric-acid works the method nearly always employed is the "*nitrometer method*," which is carried out as follows *:—

Dissolve a good-sized sample, say 20 to 30 grams, of the nitrate

---

* The nitrometer in its use for the analysis of nitrous vitriol will be described in Chap. III.

in twice its weight of water, employing a flask of known contents and heating very gently. Weigh out a quantity corresponding to about 0·4 gram $NaNO_3$ in an ordinary weighing-glass or in a tube with stopcock, as employed for testing fuming sulphuric acid (fig. 8). Run its contents into a nitrometer, either a "bulb-nitrometer," as shown in fig. 9, or, preferably, the non-graduated agitating-vessel connected with a Lunge's gas-volumeter, to be described in the next Chapter. In the latter case no observation of temperature and barometric pressure nor any reduction tables are required. Do not rinse the weighing-tube (which would dilute the liquid too much), but weigh it back as it is. Decompose

Fig. 8.

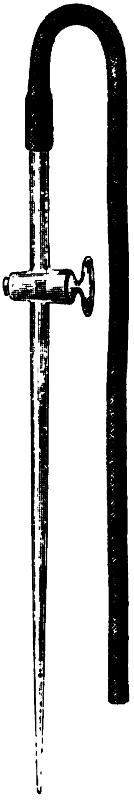
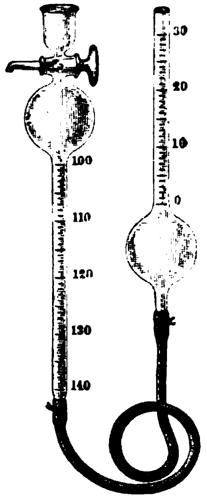


Fig. 9.



the solution within the nitrometer with a sufficient quantity of strong sulphuric acid and mercury, and measure the nitric oxide given off as will be described in the next Chapter, where also a table for reducing the readings to $NaNO_3$ will be given.

7. Nitric Acid, NO_3H.*

This may be called one of the raw materials of vitriol-making, although a manufactured product itself, in those works using it in lieu of solid nitrate of soda.

Nitric acid proper (the monohydrate) has the equivalent 63·05 ($O = 16$), and may be said to contain, as formerly expressed, 85·71 nitric anhydride (N_2O_5) and 14·29 water. Its specific gravity is 1·54 at 20°, or 1·55 at 15°. It is colourless if perfectly pure; but the strongest acid of commerce is always coloured yellow, or even red, by a partial decomposition into oxygen and nitrogen peroxide, N_2O_4 (hyponitric acid). Its boiling-point is 86° C. On boiling an acid containing a little water, at first strong acid distils over, till the boiling-point of the remainder has reached 126°, at which point the thermometer remains stationary, and an acid of constant composition for any certain pressure distils over. Exactly the same point is reached from the opposite side by distilling more dilute acids, in which case water distils over, and the remaining acid becomes more and more concentrated, till the above stationary point is reached. The acid at that point has nearly the composition $2NO_3H + 3H_2O$ (corresponding to 60 N_2O_5 and 40 H_2O) and a specific gravity of 1·42.

The following table shows the boiling-points of nitric acid of various strengths :—

Spec. grav.	Boiling-point.	Spec. grav.	Boiling-point.
1·15	104° C.	1·42	123° C.
1·20	108	1·48	115
1·30	113	1·50	99
1·35	117	1·52	86
1·40	119		

---

* Some interesting notes on the early history of manufacturing nitric acid in England are contained in Guttmann's paper, Journ. Soc. Chem. Ind. 1901, p. 7. The cost of producing 200 lbs. of acid spec. grav. 1·375 in 1771 was £8 *2s.* *2d.* without labour. See also W. P. Reid's notes, *ibid.* p. 8.

For the percentage of nitric acid for different specific gravities, Kolb (Bull. Soc. Ind. de Mulhouse, 1866, p. 412) has given a table which is now rendered obsolete by the more accurate table derived from the experiments of Lunge and Rey (Zsch. angew. Ch. 1891, p. 165). The specific gravities are taken at 15° C., referred to water of 4° and reduced to the vacuum. They refer to *chemically pure* nitric acid; commercial acid, containing nitrous acid, &c., contains less real HNO_3 at the same specific gravity.

Specific gravities at $\frac{15^\circ}{4^\circ}$.	Degrees Twadd.	100 parts by weight contain		1 litre contains kilog.	
		N_2O_5.	HNO_3.	N_2O_5.	HNO_3.
1·000	0	0·08	0·10	0·001	0·001
1·005	1	0·85	1·00	0·008	0·010
1·010	2	1·62	1·90	0·016	0·019
1·015	3	2·39	2·80	0·024	0·028
1·020	4	3·17	3·70	0·033	0·038
1·025	5	3·94	4·60	0·040	0·047
1·030	6	4·71	5·50	0·049	0·057
1·035	7	5·47	6·38	0·057	0·066
1·040	8	6·22	7·26	0·064	0·075
1·045	9	6·97	8·13	0·073	0·085
1·050	10	7·71	8·99	0·081	0·094
1·055	11	8·43	9·84	0·089	0·104
1·060	12	9·15	10·68	0·097	0·113
1·065	13	9·87	11·51	0·105	0·123
1·070	14	10·57	12·33	0·113	0·132
1·075	15	11·27	13·15	0·121	0·141
1·080	16	11·96	13·95	0·129	0·151
1·085	17	12·64	14·74	0·137	0·160
1·090	18	13·31	15·53	0·145	0·169
1·095	19	13·99	16·32	0·153	0·179
1·100	20	14·67	17·11	0·161	0·188
1·105	21	15·34	17·89	0·170	0·198
1·110	22	16·00	18·67	0·177	0·207
1·115	23	16·67	19·45	0·186	0·217
1·120	24	17·34	20·23	0·195	0·227
1·125	25	18·00	21·00	0·202	0·236
1·130	26	18·66	21·77	0·211	0·246
1·135	27	19·32	22·54	0·219	0·256
1·140	28	19·98	23·31	0·228	0·266
1·145	29	20·64	24·08	0·237	0·276
1·150	30	21·29	24·84	0·245	0·286
1·155	31	21·94	25·60	0·254	0·296
1·160	32	22·60	26·36	0·262	0·306
1·165	33	23·25	27·12	0·271	0·316
1·170	34	23·90	27·88	0·279	0·326
1·175	35	24·54	28·63	0·288	0·336
1·180	36	25·18	29·38	0·297	0·347
1·185	37	25·83	30·13	0·306	0·357

TABLE (continued).

Specific gravities at $\frac{15^\circ}{4^\circ}$.	Degrees Twadd.	100 parts by weight contain		1 litre contains kilog.	
		N_2O_5.	HNO_3.	N_2O_5.	HNO_3.
1·190	38	26·47	30·88	0·315	0·367
1·195	39	27·10	31·62	0·324	0·378
1·200	40	27·74	32·36	0·333	0·388
1·205	41	28·36	33·09	0·342	0·399
1·210	42	28·99	33·82	0·351	0·409
1·215	43	29·61	34·55	0·360	0·420
1·220	44	30·24	35·28	0·369	0·430
1·225	45	30·88	36·03	0·378	0·441
1·230	46	31·53	36·78	0·387	0·452
1·235	47	32·17	37·53	0·397	0·463
1·240	48	32·82	38·29	0·407	0·475
1·245	49	33·47	39·05	0·417	0·486
1·250	50	34·13	39·82	0·427	0·498
1·255	51	34·78	40·58	0·437	0·509
1·260	52	35·44	41·34	0·447	0·521
1·265	53	36·09	42·10	0·457	0·533
1·270	54	36·75	42·87	0·467	0·544
1·275	55	37·41	43·64	0·477	0·566
1·280	56	38·07	44·41	0·487	0·568
1·285	57	38·73	45·18	0·498	0·581
1·290	58	39·39	45·95	0·508	0·593
1·295	59	40·05	46·72	0·519	0·605
1·300	60	40·71	47·49	0·529	0·617
1·305	61	41·37	48·26	0·540	0·630
1·310	62	42·06	49·07	0·551	0·643
1·315	63	42·76	49·89	0·562	0·656
1·320	64	43·47	50·71	0·573	0·669
1·325	65	44·17	51·53	0·585	0·683
1·330	66	44·89	52·37	0·597	0·697
1·335	67	45·62	53·22	0·609	0·710
1·340	68	46·35	54·07	0·621	0·725
1·345	69	47·08	54·93	0·633	0·739
1·350	70	47·82	55·79	0·645	0·753
1·355	71	48·57	56·66	0·658	0·768
1·360	72	49·35	57·57	0·671	0·783
1·365	73	50·13	58·48	0·684	0·798
1·370	74	50·91	59·39	0·698	0·814
1·375	75	51·69	60·30	0·711	0·829
1·380	76	52·52	61·27	0·725	0·846
1·385	77	53·35	62·24	0·739	0·862
1·390	78	54·20	63·23	0·753	0·879
1·395	79	55·07	64·25	0·768	0·896
1·400	80	55·97	65·30	0·783	0·914
1·405	81	56·92	66·40	0·800	0·933
1·410	82	57·86	67·50	0·816	0·952
1·415	83	58·83	68·63	0·832	0·971
1·420	84	59·83	69·80	0·849	0·991
1·425	85	60·84	70·98	0·867	1·011
1·430	86	61·86	72·17	0·885	1·032
1·435	87	62·91	73·39	0·903	1·053
1·440	88	64·01	74·68	0·921	1·075

TABLE (continued).

Specific gravities at $\frac{15^\circ}{4^\circ}$.	Degrees Twadd.	100 parts by weight. contain		1 litre contains kilog.	
		N_2O_5.	HNO_3.	N_2O_5.	HNO_3.
1·445	89	65·13	75·98	0·941	1·098
1·450	90	66·24	77·28	0·961	1·121
1·455	91	67·38	78·60	0·981	1·144
1·460	92	68·56	79·98	1·001	1·168
1·465	93	69·79	81·42	1·023	1·193
1·470	94	71·06	82·90	1·045	1·219
1·475	95	72·39	84·45	1·068	1·246
1·480	96	73·76	86·05	1·092	1·274
1·485	97	75·18	87·70	1·116	1·302
1·490	98	76·80	89·60	1·144	1·335
1·495	99	78·52	91·60	1·174	1·369
1·500	100	80·65	94·09	1·210	1·411
1·501	—	81·09	94·60	1·217	1·420
1·502	—	81·50	95·08	1·224	1·428
1·503	—	81·91	95·55	1·231	1·436
1·504	—	82·29	96·00	1·238	1·444
1·505	101	82·63	96·39	1·244	1·451
1·506	—	82·94	96·76	1·249	1·457
1·507	—	83·26	97·13	1·255	1·464
1·508	—	83·58	97·50	1·260	1·470
1·509	—	83·87	97·84	1·265	1·476
1·510	102	84·09	98·10	1·270	1·481
1·511	—	84·28	98·32	1·274	1·486
1·512	—	84·46	98·53	1·277	1·490
1·513	—	84·63	98·73	1·280	1·494
1·514	—	84·78	98·90	1·283	1·497
1·515	103	84·92	99·07	1·287	1·501
1·516	—	85·04	99·21	1·289	1·504
1·517	—	85·15	99·34	1·292	1·507
1·518	—	85·26	99·46	1·294	1·510
1·519	—	85·35	99·57	1·296	1·512
1·520	104	85·44	99·67	1·299	1·515

Correction of the observed specific gravities for temperatures a little above or below 15° C.

			Add for −1° C. Deduct for +1° C.
With spec. grav.	between	1·000—1·020	0·0001
,,	,,	1·021—1·040	0·0002
,,	,,	1·041—1·070	0·0003
,,	,,	1·071—1·100	0·0004
,,	,,	1·101—1·130	0·0005
,,	,,	1·131—1·160	0·0006

Correction of the observed specific gravities (continued).

With spec. grav.	between	1·161—1·200	0·0007
,,	,,	1·201—1·245	0·0008
,,	,,	1·246—1·280	0·0009
,,	,,	1·281—1·310	0·0010
,,	,,	1·311—1·350	0·0011
,,	,,	1·351—1·365	0·0012
,,	,,	1·366—1·400	0·0013
,,	,,	1·401—1·435	0·0014
,,	,,	1·436—1·490	0·0015
,,	,,	1·491—1·500	0·0016
,,	,,	1·501—1·520	0·0017

Loring Jackson and Wing, and a little later on R. Hirsch (Chem. Zeit. 1888, p. 911), have shown that the presence of *lower oxides of nitrogen* in nitric acid has a considerable influence on its specific gravity. Thus the first runnings from a distillation possessed a specific gravity =1·62, but contained 12 per cent. by weight of HNO_2. Hirsch assumes (without strict proof) that each per cent. of HNO_2 raises the specific gravity by 0·01. If this is correct, an acid of sp. grav. 1·44, but containing 1 per cent. HNO_2, really contains only 99 per cent. of HNO_3 of spec. grav. 1·43. Now 100 grams of pure acid of 1·44 are=74·4 grams HNO_3, but 99 grams of 1·43 only =71·0; hence the 1 per cent. of HNO_2 present makes a difference of 3·4 per cent. of HNO_3 in the real strength, compared with the apparent strength as taken from the specific-gravity tables.

This subject has been more accurately investigated by Lunge and Marchlewski. From their paper (Zsch. f. angew. Ch. 1892, p. 10) I give the following table, showing this influence in the case of nitric acid of spec. grav. 1·4960 (at $\frac{15^\circ}{4^\circ}$) :—

N_2O_4 per cent.	Alteration of spec. grav. by N_2O_4.	N_2O_4 per cent.	Alteration of spec. grav. by N_2O_4.
0·25	0·00050	6·55	0·04475
0·50	0·00075	7·00	0·04650
0·75	0·00150	7·25	0·04720
1·00	0·00300	7·50	0·05000
1·25	0·00475	7·75	0·05165
1·50	0·00675	8·00	0·05325
1·75	0·00775	8·25	0·05500
2·00	0·01050	8·50	0·05660
2·25	0·01250	8·75	0·05825
2·50	0·01425	9·00	0·06000
2·75	0·01625	9·25	0·06160
3·00	0·01800	9·50	0·06325
3·25	0·01985	9·75	0·06500
3·50	0·02165	10·00	0·06600
3·75	0·02350	10·25	0·06815
4·00	0·02525	10·50	0·06975
4·25	0·02690	10·75	0·07135
4·50	0·02875	11·00	0·07300
4·75	0·03050	11·25	0·07450
5·00	0·03225	11·50	0·07600
5·25	0·03365	11·75	0·07750
5·50	0·03600	12·00	0·07850
5·75	0·03775	12·25	0·08050
6·00	0·03950	12·50	0·08200
6·25	0·04175	12·75	0·08350
6·50	0·04300		

Saposchnikoff (Chem. Centralbl. 1900, ii. p. 708, and 1901, ii. p. 1330) has studied the conditions of equilibrium between HNO_3, HNO_2, and NO, *i. e.* the formation of HNO_3 and NO from HNO_2, and the reduction of HNO_3 by NO to HNO_2.

The oxidizing properties of nitric acid are well known and cannot be described in detail here; but it should be mentioned that an acid containing the lower oxides of nitrogen, such as the "red fuming nitric acid," has even more strongly oxidizing properties than the pure acid, and this helps to explain some points in the theory of the formation of sulphuric acid, as we shall see in a subsequent chapter.

Manufacture of Nitric Acid.—This acid has been known since the times of Geber, in the eighth century; and Raymundus Lullus in 1225 taught how to prepare it by distilling a mixture of clay and saltpetre. Now-a-days it is always made by distilling nitrate of soda with sulphuric acid, an excess of the latter acid beyond the theoretical quantity being used in practice. By the equation: $2NaNO_3 + H_2SO_4 = 2HNO_3 + Na_2SO_4$, in theory 85 parts of $NaNO_3$ require 49 parts of SO_4H_2, and yield $63NO_3H$ along with $71Na_2SO_4$; this comes to the same as 57·6 parts of SO_4H_2, or, say, 60 parts of ordinary strong oil of vitriol (with 95 per cent. of SO_4H_2) to 100 parts of 95-per-cent. nitrate. If these proportions are used, a portion of the nitric acid is always decomposed into O and N_2O_4, and red fuming acid is obtained. This arises from the fact that the above equation is only realized at a high temperature, whilst at less elevated temperatures sodium bisulphate is formed: $NaNO_3 + H_2SO_4 = HNO_3 = NaHSO_4$. Moreover, the presence of strong sulphuric acid, owing to its attraction for the elements of water, has a tendency to split up some HNO_3 into H_2O and N_2O_5, the latter compound being at once decomposed into N_2O_4 and O. To avoid the loss involved in this operation, generally more dilute nitric is produced by employing weaker sulphuric acid, say of 140°-148° Tw., and more than the theoretical quantity of it, generally from 20 to 30 per cent. in excess of the simple equivalent. In this case the admixture of a certain quantity of sodium bisulphate makes the residue of distillation much more easily fusible and facilitates its removal from the retorts. When the acid is made at factories where salt is decomposed, even more sulphuric acid than the above is generally employed, as the excess is not lost, the residual "cylinder-cake" or "nitre-cake" being regularly mixed with the salt to be decomposed in the sulphate-pans; in this case as much sulphuric acid is saved as corresponds to the bisulphate contained in the cylinder-cake.

Nitric acid was formerly made in glass retorts, which are practically obsolete now, cast-iron retorts being universally employed. The retorts belong mainly to two different types—horizontal cylinders, charged sideways, and pots or stills, charged from the top.

The ordinary type of French cylinder apparatus, used in many places outside of France as well, is represented in figs. 10 and 11 on a scale of 1 : 25.

The ends of the cylinders are here exposed to the air and consist of cast-iron disks, 1½ inch thick, cemented into the rebates cast on to the ends of the cylinder by the usual rust cement (100 iron filings, 5 flowers of sulphur, 5 sal-ammoniac), or by a mixture of this with ground fire-bricks and the like. At all events the back end is fixed in this way, and is provided with a pipe for

Fig. 10.

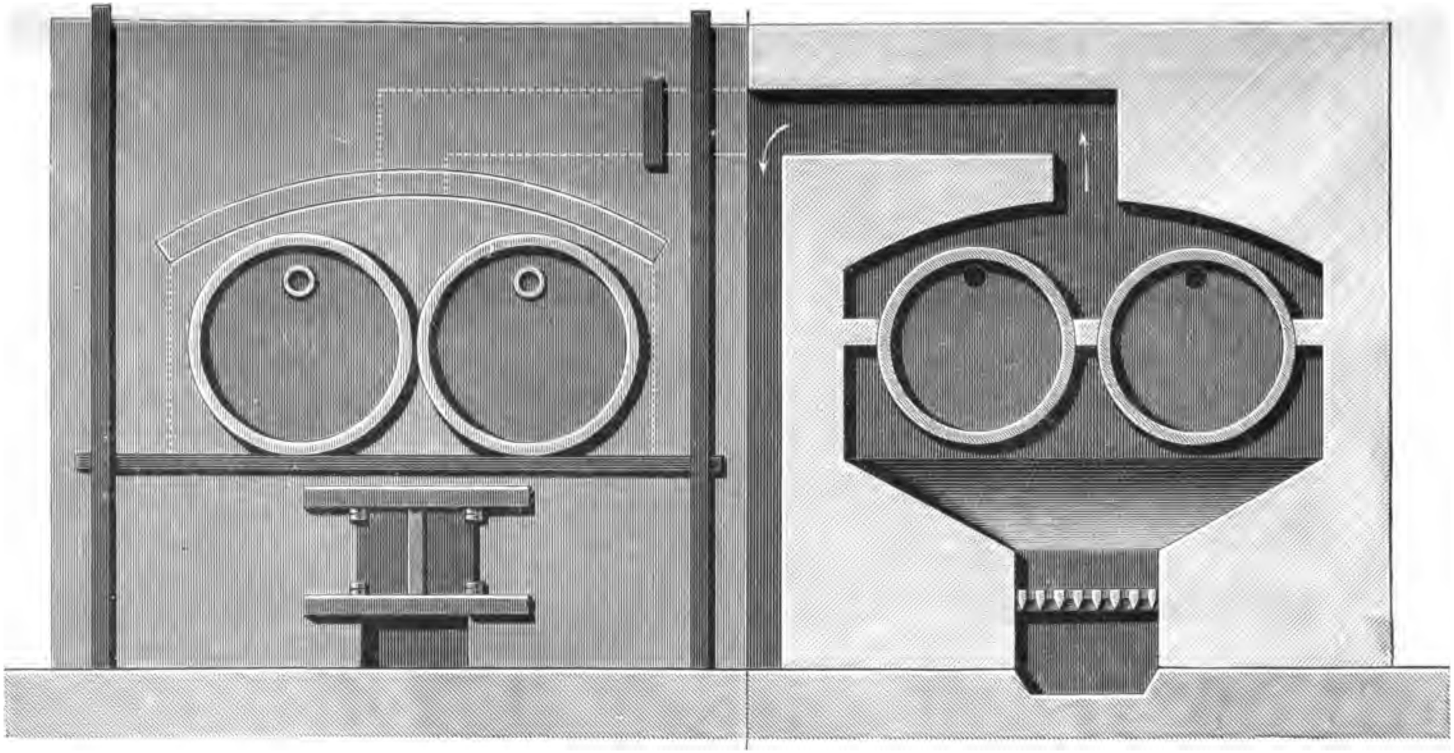
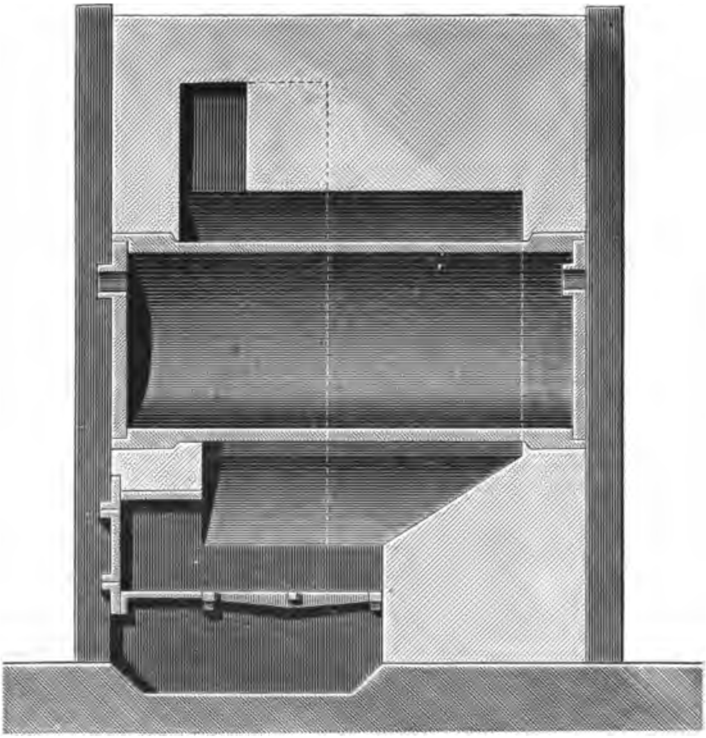


Fig. 11.



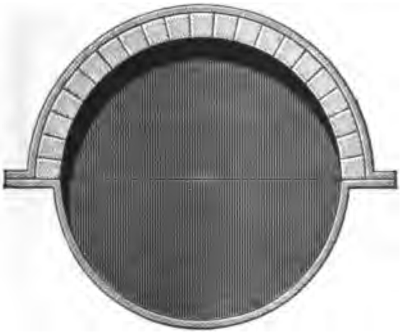
taking away the vapours; the other end is made to take off and serves for charging the nitre and discharging the residue. A hole and S-shaped funnel in the man-lid allow of running in the sulphuric acid. These cylinder-ends cause a good deal of cooling, and consequently a loss of fuel, which can be avoided to a great extent if they are not made of iron but of a single stone flag each; the charging end also remains fixed in this case, the nitre being charged through a small general opening in it, and the residue being run off in a liquid state through a pipe generally closed by a ground-in iron stopper. A little more sulphuric acid is employed in this case, so as to obtain a very fluid mass at the end. If sulphuric acid of 144° Tw. is employed, the receivers will contain nitric acid of 77° to 82° Tw.; if weaker acid is desired, a little water is put into the receivers. The strongest acid, of 100° Tw., can only be made from strong vitriol and dried nitrate.

At first the cylinders are fired rather strongly; but as soon as the first receivers get warm the fire is slackened, and during 18 hours is kept so that of eight receivers only the first five are warm to the touch. If the heat gets up too high, the contents of the retort may boil over, and far more ruddy vapours will be formed. The end of the reaction is known by the cooling of the receivers; then the fire is increased again for a little time, and at last is allowed to go down.

In regular work, there are some red vapours at first, but much less with rather weaker acid (say 135° Tw.) than with stronger acid. At the end the red or yellow vapours appear again and last up to the finish.

The cylinders are sometimes cast so that their upper half can be protected against the attack of the acid by lining it with acid-proof bricks (see fig. 12); but some believe that this does more harm than good, as the upper part of the metal cylinder is all the less acted upon by the nitric acid the hotter it becomes.

Fig. 12.



A more perfect form of cylinders is that employed at the Griesheim works, and shown in full detail in figs. 13 to 16 with all the measurements marked in centimetres *.

These retorts work off 8 cwt. of nitre per 24 hours, with an expenditure of 2½ cwt. of coal or very little more, inclusive of the time of filling and emptying. In case of need, 25 per cent. more can be charged, without fear of boiling over, with careful work.

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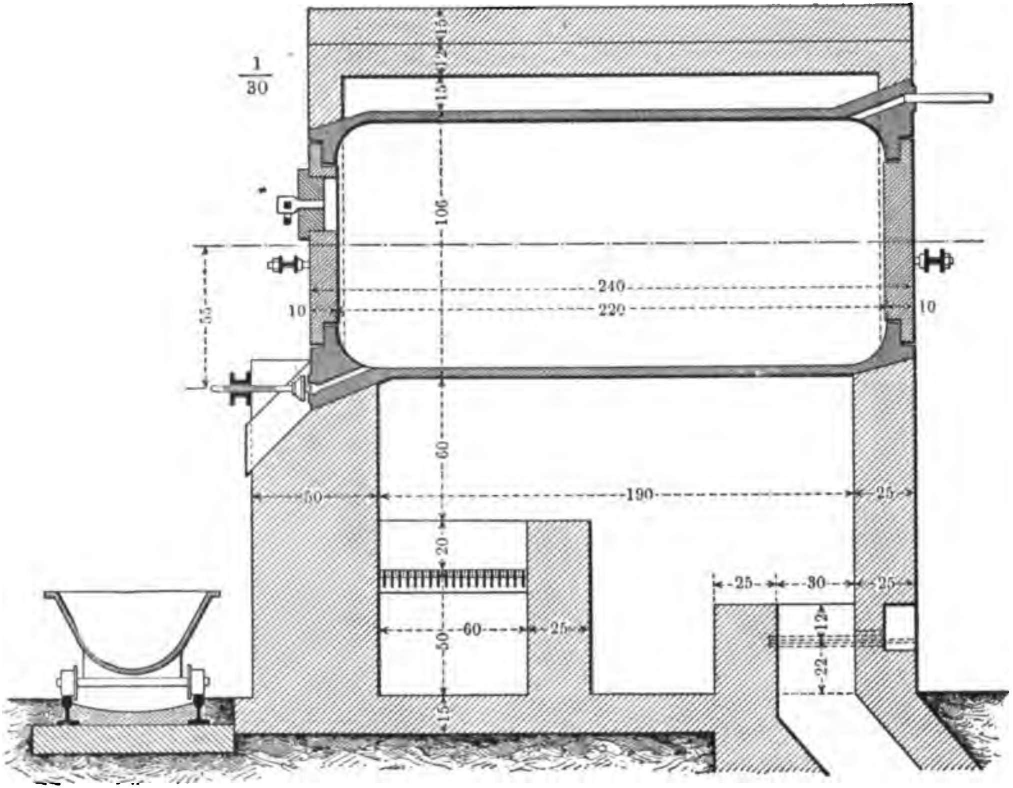
* These figures are taken from Häussermann's article "Nitric Acid," in Muspratt-Bunte's Enc. d. Techn. Chemie, 4th ed. vii. p. 651 *et seq.* Some notes from this article are also given in the following pages.

Fig. 13.



Longitudinal section.

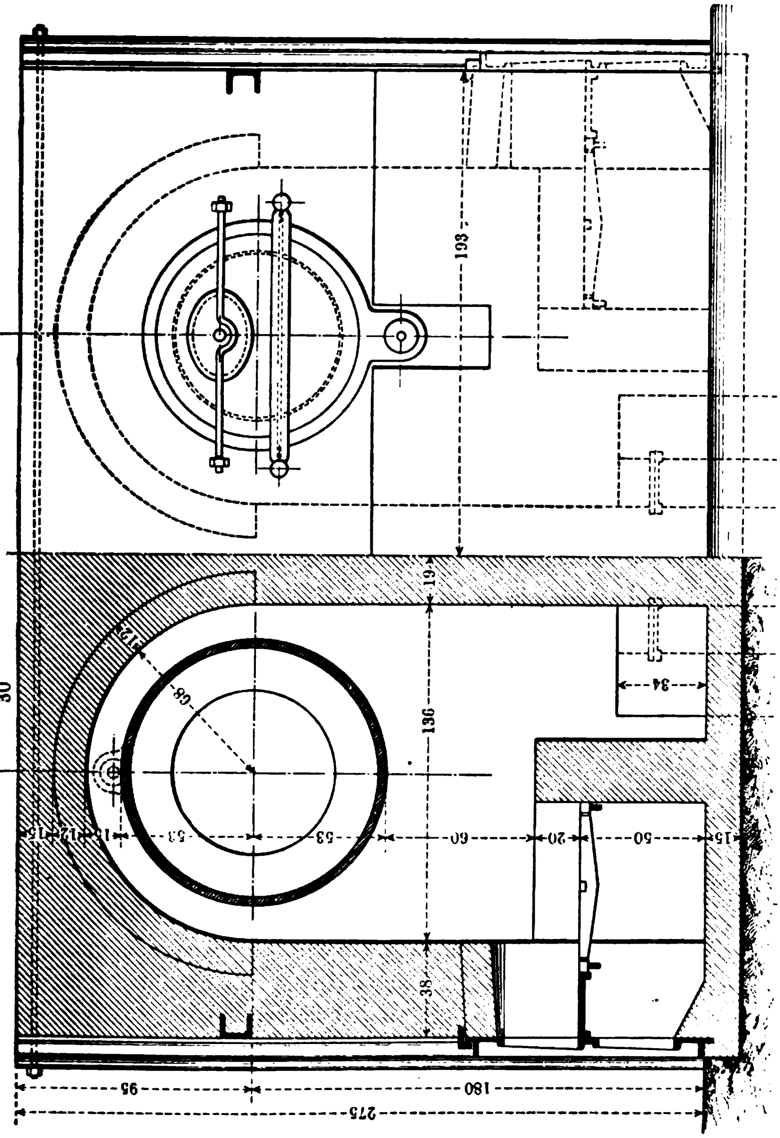


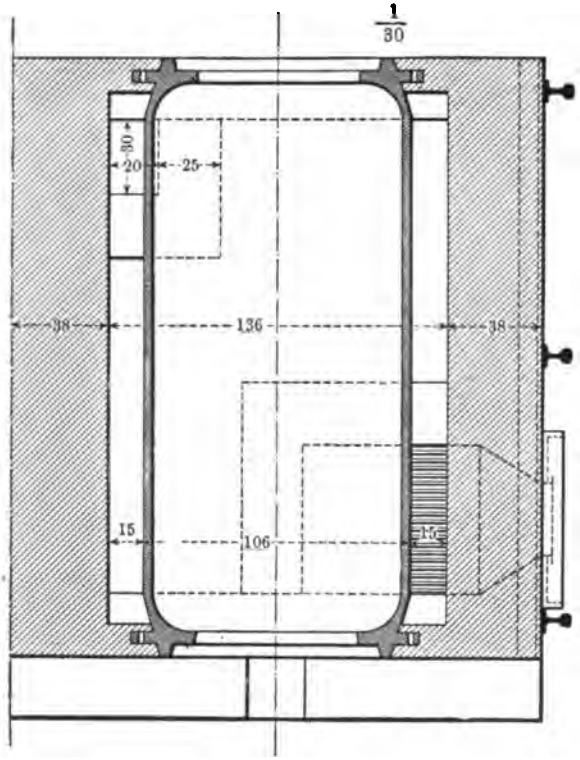
Fig. 14. $\frac{1}{30}$

Sectional elevation.

Fig. 15.

Front elevation.

Fig. 16.



Sectional plan.

Such boiling over occurs more easily with strong sulphuric acid (of 1·84 spec. grav.) than with weaker acid (140° Tw.). The setting is so arranged that the fire-gases entirely surround the cylindrical part, and the ends are made of sandstone slabs, cemented and kept in their places by iron bars pressing against them on the outside. In this kind of apparatus no corrosion takes place, wherefore the arrangement shown in fig. 12 (p. 107) is quite unnecessary. The exit opening continues into a glass tube, forming connection with the condensing-apparatus. The arrangement for running off the nitre-cake is made quite clear in fig. 13.

The objection sometimes made to cylindrical retorts, that they do not easily permit the manufacture of the strongest nitric acid, is refuted by the experience of many years at the various works belonging to the Griesheim Company.

Vol. I. *Sulphuric Acid.*

The other class of retorts, taking the shape of pots or stills, is either entirely surrounded by the fire, or with its top exposed to the air. The former kind, as employed in France for very strong nitric acid, is shown in fig. 17. It consists of cast-iron pots of from 4 to 5 feet diameter and equal height, and a metal thickness of 1¾ to 2 inches (rather thicker at the bottom). There is a wide neck *a* at the top, closed by a lid, fastened on with a suitable cement, *e. g.* a mixture of clay and gypsum. There is a tube *b* for carrying away the gas, either coming out perpendicularly at the top, as shown here, or bending away horizontally, as in a laboratory retort; this tube should be lined with an earthenware tube as far as it is at all liable to cool down below the point where the metal can be acted upon by nitric acid. Another tube *c* serves for introducing the sulphuric acid; this is preferable to running it in through the neck *a*, after charging the nitre. Sometimes there is no pipe provided for running out the liquid residue, but it is better to have one, as shown at *d*, and to protect this tube against the direct action of the fire by a fire-proof covering. Where this is not provided, the liquid residue must be ladled out through *a* at the close of the operation, which is a disagreeable proceeding. The pot is set in a furnace so that it is altogether surrounded by the fire, even at the top, to which access is afforded for charging by lifting off a fire-clay slab, or a metal plate filled with ashes, as shown at *e*. By this means a saving of fuel is effected, and the equal heating of the retort causes it to stand the action of the nitric acid very well. A pot 5 feet wide and 5 feet high takes a charge of 9 cwt. of nitre, and requires from 16 to 18 hours to work this off, including the time for charging and emptying. Of this time, one hour may be reckoned for charging and making the joints, six hours for the first stage, where red fumes appear, about as much for the second stage, where the vapours are almost colourless, and four or five hours for the last stage, where the temperature has to be raised much higher, the yellow and red vapours appear again and more water comes over with the acid.

That kind of pot where the top (with the small hole) is exposed to the air is shown on a scale of 1 : 60 in fig. 18. It forms part of the Valentiner vacuum system to be described below. The pot, for a charge of a ton of nitre, is composed of two parts. The outlet-pipe for the nitre-cake runs almost horizontally, so that it is easily cleaned. The gas-pipe first enters a small receiver, destined to keep back any froth carried over. Such a vacuum retort is finished in 12 hours, with about 4 cwt. of coal per ton of nitre.

Fig. 18.

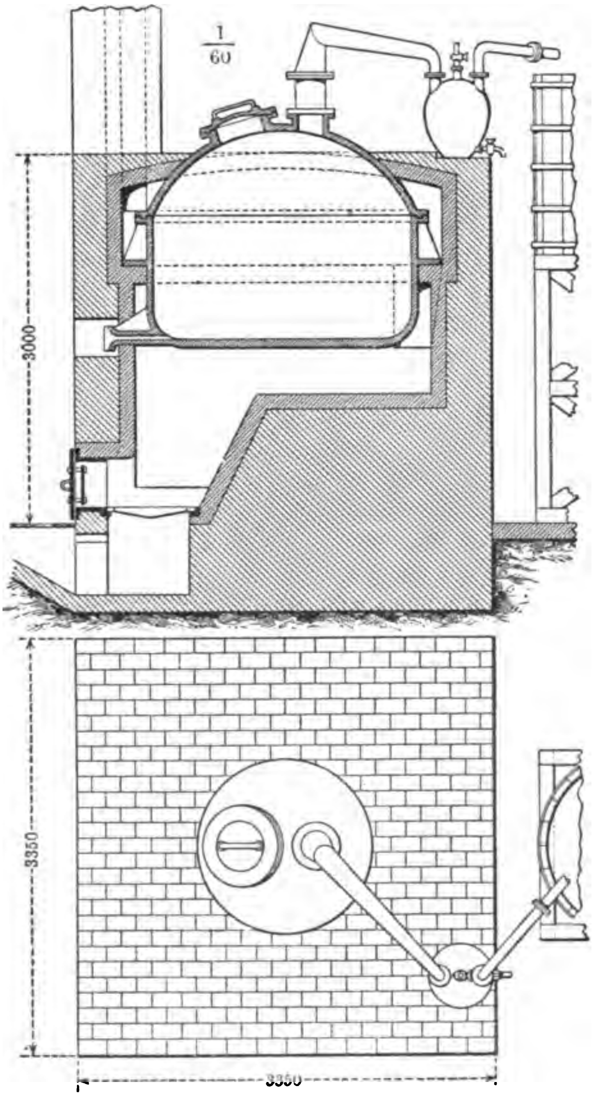
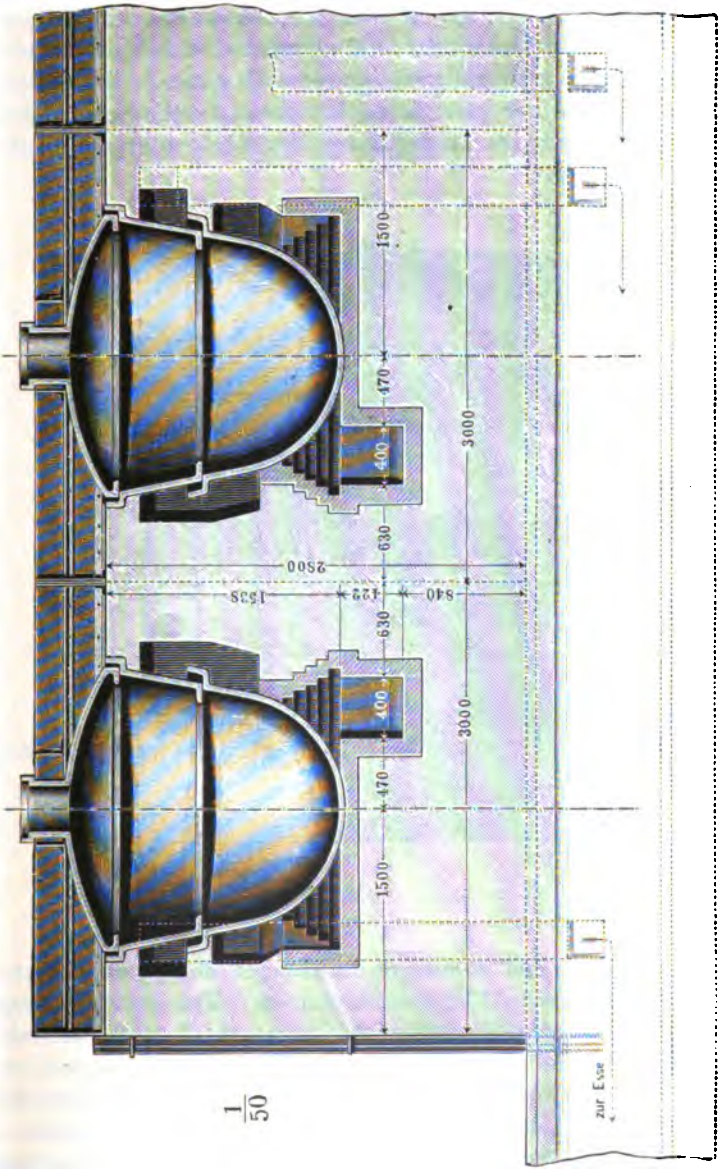
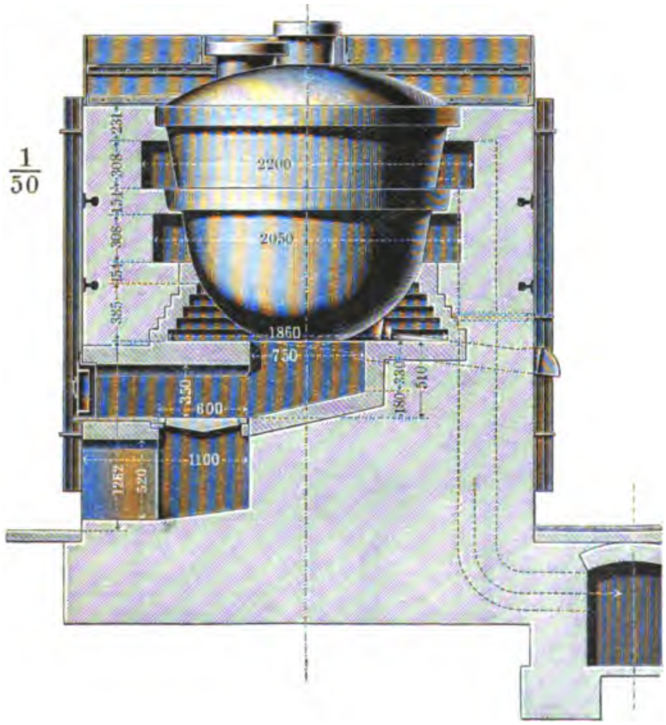


Fig. 10.


1500
470
400
3000
630
2500
1538
122
840
630
400
3000
470
1500
zur Esse
1/50

Figs. 19, 20, and 21, from drawings which I owe to the kindness of Mr. H. H. Niedenführ, show the kind of still employed by Mr. O. Guttmann in connexion with his condensing-plant, but of course applicable in every other case. The drawings are to scale and are clear enough without further explanations. The brick setting, as arranged by Mr. Niedenführ, has had an excellent effect, and admits of finishing a charge of 12 cwt. in 24 hours with only 17 per cent. of coal. The internal flanges have the effect of diverting the contents of the pot, when frothing, towards the centre, and of preventing any acid condensing from running down the sides. These retorts have been found specially useful for making a maximum of strong acid.

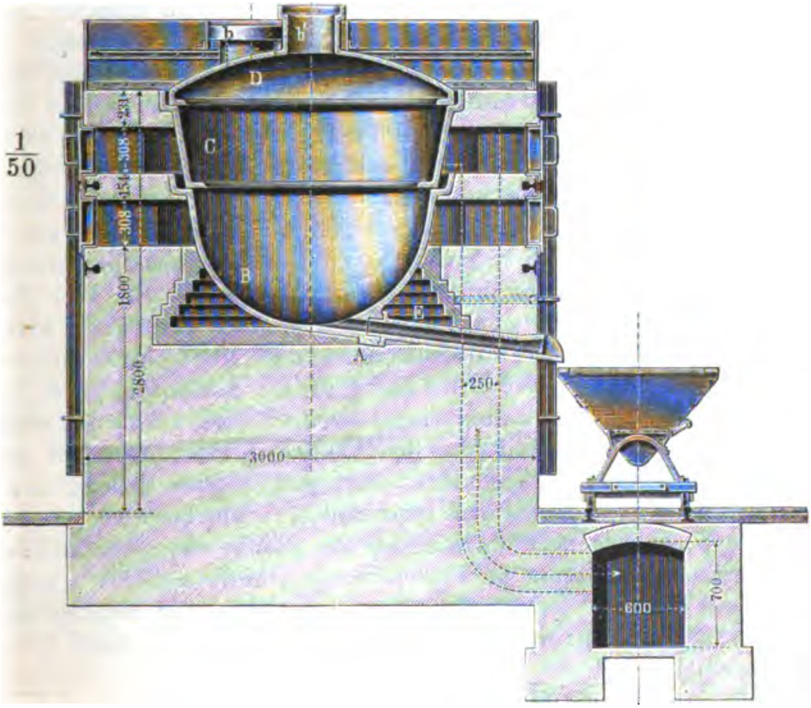
Fig. 20.



Usually it is preferred to cast such conical pots in one piece (like caustic-soda pots), and to set them so that the cover projects over the brickwork. In order to keep the cover sufficiently hot, it is covered by a layer of ashes or by bricks; the drying of the nitre in this case is equally performed by the waste heat of the fire, but in a separate place at the end of the retort-bench.

At some works they use large semicylindrical troughs of cast metal with broad flanges and a vertical rim all round, in order to cover them by a brick arch or a stone slab. At others they employ large pots with rounded bottom, lying on their side: the open end, which forms part of the front of the furnaces, being closed by a stone slab. Neither of these forms has found very much favour elsewhere.

Fig. 21.



Prentice (Engl. pat. 6960, 1893) carries on the process in a continuous manner. The nitre is mixed with sulphuric acid outside the retort, preferably in a kind of mortar-mill (according to patent No. 8902, 1893, a large excess of sulphuric acid should be employed and the residue subsequently used for the manufacture of superphosphate). The mud thus produced is conveyed into a heated chamber in which the nitrate dissolves in the sulphuric acid, but no nitric acid is as yet split off [?]; here chlorine and nitrogen tetroxide are liberated and escape into a condensing-apparatus. Owing to this the nitric acid is later on free from volatile impurities [?]. The mixture is now charged into the retort, which has an oblong section and is divided into a number of separate chambers by partitions starting from the cover and not reaching entirely to the bottom. Above each chamber the cover is provided with a head and vapour-pipe. The retort is heated from below, and the fire-gas subsequently travels round the sides. The mixture coming from the heating-chamber enters the first chamber of the retort, where it begins to boil and gives off a large quantity of strong nitric acid mixed with a little nitrogen tetroxide. The mixture now, without ceasing to boil, flows on from chamber to chamber, giving off pure nitric acid, which gets weaker and weaker in the following chambers. In the last chamber, placed immediately above the fire, the temperature is highest; here the last nitric acid is driven off, together with much water and a little sulphuric acid, and the nitre-cake is drawn off, free from the nitrate. By this method $\frac{2}{3}$ of the fuel and $\frac{4}{5}$ of the condensing-plant [?] can be saved. A still producing 4 tons per week weighs less than two tons.—A communication by Prentice in the 'Journal of the Society of Chemical Industry,' 1894, p. 323, gives nothing new. In discussing it doubts were expressed as to whether that process is applicable at such works where the residue cannot be utilized for the manufacture of superphosphate, as it contains a large excess of acid. Indeed, this extra quantity of acid required for working that otherwise very ingenious process has made it an economical failure.

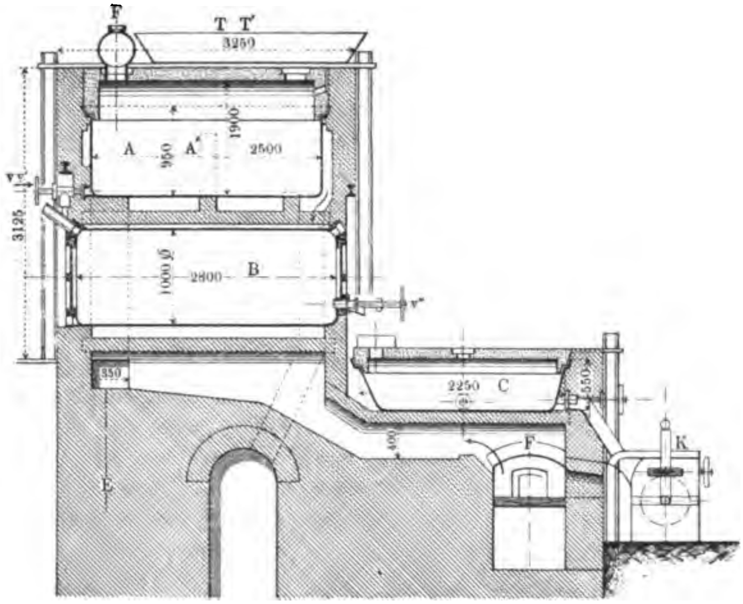
Uebel (patents of the Chemische Fabrik Rhenania, E. P. 27240, 1898, and 3305, 1901) proceeds in a novel way for the manufacture of nitric acid. The nitre-cake, running out at a high temperature from the retorts, is mixed with sulphuric acid of about 1·71 spec. grav. in such proportions that a "polysulphate" is formed, the water being evaporated by the heat remaining in the nitre-cake. This polysulphate, of a composition $=NaH_3(SO_4)_2$, serves instead of fresh sulphuric acid for manufacturing the next batch of nitric acid, in which case the latter is obtained of the highest strength, just as if the strongest sulphuric acid had been employed.

Of course the fresh nitre-cake formed from the second operation amounts to much more than that from the first; therefore a portion of it is set aside in the ordinary manner, and the remainder is again employed for making nitric acid. The practical work carried out with this process has led to the construction of a new and original style of retorts, which may be very usefully adopted even when nitrate of soda is to be decomposed in the ordinary way by sulphuric acid, not by "polysulphate."

The principal advantages of the new process are: that the alternate heating and cooling of the apparatus is avoided, which produces a saving in fuel and prolonged duration of the plant; that there is not the same inequality of the nitric acid as is produced during the period of working off a retort on the old system; that a much smaller and consequently much cheaper plant and only half of the ordinary ground-space are required for the same output, both for distillation and condensation (the Uebel plant may be combined with any of the systems of condensation to be described below); that there is less labour required; and that the strongest acid can be made by means of ordinary sulphuric acid 140° Tw., as its water is evaporated free of expense in the formation of the polysulphate—"waste-acid" from nitrating processes being equally fit for employment.

The Uebel process is illustrated in figs. 22 to 24. Two parallel retorts A, A′ (consisting of a cast-iron bottom piece and a stone or stoneware cover) are alternately charged with nitrate of soda and the requisite quantity of liquid "polysulphate" (or else, if there is a sufficient quantity of *strong* acid at disposal, *e.g.* where manufacturing by contact processes, directly with such acid). The heating is performed by the waste fire-gases of the lower retort B, a temperature of 170° to 200° C. being thus attained in A and A′. When most of the nitric acid has been expelled, the contents of A and A′ are let down into retort B, where the last portion of nitric acid is liberated, at a temperature of about 300° C. The contents of B have, of course, been previously run out, but never completely, leaving always a stock of hot liquid "bisulphate" in the retort. The bisulphate (nitre-cake) is run from B into the cast-iron pan C, where it is mixed with previously heated sulphuric acid of about 140° Tw. (or with waste acid from nitrating processes of equal strength) in the proportion of forming a tetrasulphate, H_2SO_4, $NaHSO_4$. In consequence of the high temperature

Fig. 22.


F
T T'
3250
1900
A
A'
950
2500
V'
3125
1000 Ø
2800
B
V''
350
E
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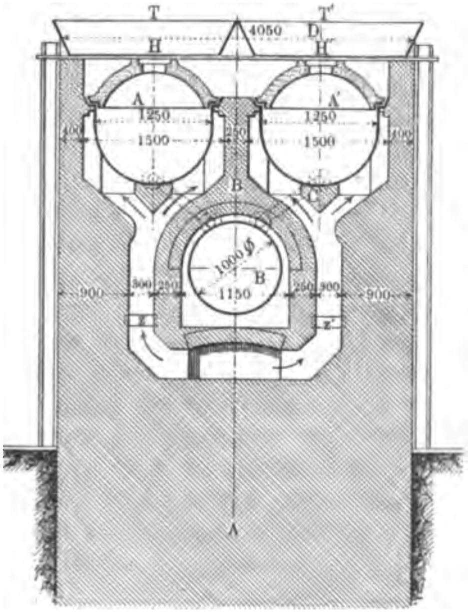
C
550
400
F
K

Fig. 23.


T
T'
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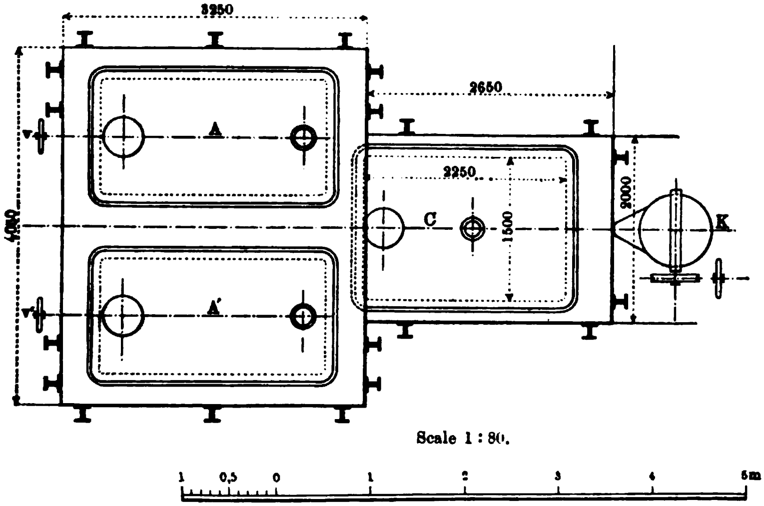
900
Z
Z'
A

of the liquid nitre-cake, the water present in the fresh sulphuric acid is evaporated (together with any nitric acid present in waste acids, if such are employed) and is carried away by a pipe, or a vapour hood, not shown in the drawing. Half of the "polysulphate" formed in C is employed for a fresh operation in A, A′, the other half being at disposal for any outside utilization in lieu of highly concentrated acid. If such utilization is not possible, half of the nitre-cake is run out from C *before* adding fresh sulphuric acid and only the other half is employed for making "polysulphate," the unemployed half being utilized in the manner followed in other cases.

Fig. 24.



(An English patent by Claes, No. 1072, 1900, describes the manufacture of such "polysulphates" from nitre-cake and sulphuric acid as a commercial article.)

The flame of the hearth F first heats retort B, which is protected by an arch, and then, according to the position of the damper, either A or A′. *v*, *v*′ are valves for discharging the contents of A, A′ into B ; *v*″ another valve for discharging B into C, placed high enough to leave a stock of liquid nitre-cake in B.

After heating-up, A is charged with 8 cwt. nitrate of soda, previously dried on the shallow basins T, T′ on the top of the furnace. The charging is performed through manholes H, H′, which are afterwards closed by covers and kept tight by nitrate of soda heaped upon them. Then fused polysulphate is gradually run in through a swan-neck pipe from the tilting-box K, previously lifted to the top of the furnace. This polysulphate will be at a temperature of about 120° or 130°, and must therefore be gradually introduced within from half an hour to an hour, so as to avoid a tumultuous evolution of nitric acid. Of course, in lieu of this, fresh acid can be employed, as stated above. During the introduction of the hot polysulphate damper *z* is closed and *z*′ is opened; when finished, *z* is opened so that the fire-gases play upon A. When the temperature has risen to about 170°, nearly all HNO_3 has been driven out; the thin, liquid melt contains a little nitrate and all the water introduced with the nitrate and the polysulphate or fresh acid. It is now slowly run through valve *v* into retort B, where it meets with a stock of hot bisulphate. Here, without the frothing taking place in the old, directly fired, retorts, the last nitric acid and the water is drawn off within a very short time. The contents of B remain there until the contents of A′ (which has been charged and worked in the meantime) are ready to be run off, which takes from 3½ to 4 hours. Then B is discharged into C, where fresh acid is run in as before described, so that room is made in B for receiving the contents of A′. A in the meantime has been left empty for an hour, damper *z* being closed, in order to cool down. Now the polysulphate is run out of C into the tilting-box K, which is hoisted up to serve as before. Thus a charge of 8 cwt. of nitrate can be worked off in each of the retorts A and A′ every four hours.

A good *cement* for permanent joints against nitric acid in the retorts consists of 10 parts powdered volvic lava, 7 iron filings, 7 powdered brimstone, 7 fire-clay, 10 ground fire-bricks, moistened with as little water as possible. If carefully stemmed into the joint, it becomes very hard.

Cement for the earthenware pipes, &c., in the condensing-apparatus can be made from 5 parts hot linseed-oil, 2 parts brimstone, 2 parts india-rubber scraps, and enough sulphate of baryta to produce a thick paste which is employed in the hot state.

The most universally employed cement for nitric acid (and other acids) is *asbestos cement.* Guttmann gives the following prescription for preparing it:—1 part silicate of soda is dissolved in 19 parts water [or, which is preferable, the usual 33 per cent. solution is diluted with 8 times its volume of water] and asbestos powder is kneaded with it in small quantities at a time, until a tough paste is obtained. Should a cement be required which will become very hard, a little finely powdered barium sulphate is mixed with it; but this is not desirable where pipes have to be changed, as the cement cannot be removed without risk of damaging the pottery. If too little water is used from the first, the water absorbed by the cement will cause it to swell and to burst the sockets. The cement is applied in small bits, and tightly pressed in by means of a piece of wood with a blunt-ended tool. The surface is flattened and moistened with some silicate of soda solution. If the putty in the sockets shrinks, about $\frac{3}{8}$ inch of it is raked out and fresh cement put in.

Asbestos cement must never be treated with pure water to begin with, but with acid or acid fumes, in order to ensure its setting by the separation of silica.

The *gases and vapours evolved during the working of the retorts*, apart from the vapour of nitric acid itself, consist of aqueous vapour, nitrogen peroxide, hydrogen chloride (which is, however, almost entirely converted into the following gases), chlorine, nitrosyl chloride, and a little iodine. HCl and the gases derived from it (NOCl and Cl) are principally formed at the commencement, through the decomposition of sodium chloride; but towards the end they appear again owing to the decomposition of perchlorate. All of these impurities are dissolved by cold nitric acid, and hence occur in ordinary, "unbleached" nitric acid.

Volney (Journ. Amer. Chem. Soc. 1891, xiii. p. 246) showed that the frothing in the ordinary nitric-acid process takes place only in the last stage, when the strong acid has passed over and when the last portion of the nitre is suddenly acted upon, with formation of weaker acid. At this period practically only $NaHSO_4$ is in the retort besides $NaNO_3$.

Later on (ibid. 1901, p. 489) Volney returned to this subject, with the following results. During the first period of the process, when the temperature of the retort is not above 100°, the compound $NaH_3(SO_4)_2$ is formed, which Volney calls "trisulphate" (it is really a tetrasulphate and identical with Uebel's "polysulphate," p. 117), by the reaction:

$$NaNO_3 + 2H_2SO_4 = NaH_3(SO_4)_2 + HNO_3.$$

The second period sets in at 100° and ends at 121°; here the principal reaction is:

$$NaNO_3 + NaH_3(SO_4)_2 = 2NaHSO_4 + HNO_3.$$

During the first period pure nitric acid, boiling between 81° and 88°, distils over. During the second period the HNO_3 begins to decompose into lower oxides and H_2O, so that more dilute acid must now be formed.

Later again (Journ. Soc. Chem. Ind. 1891, p. 544; comp. also Journ. Amer. Chem. Soc. 1902, p. 226), Volney states that the first phase, where acid of 77°–90° boiling-point comes over, takes place at a temperature of 97°–122°; the second phase, where acid of spec. grav. 1·505, boiling at 94°–100°, comes over, requires a temperature in the retort of 130°–165°. Above this the decomposition of HNO_3 sets in and yellow acid comes over. All this refers to working under ordinary pressures. When, however, working at reduced pressure on the Valentiner system (originally proposed by me, comp. *infra*), say at 300 mm., the first stage runs from 55°–100°, the boiling-point of the strongest acid at that pressure being only 45°–75°; the second stage, where the polysulphate acts upon more nitrate, begins at 100° and is finished at 120°, instead of at 165° at ordinary pressure.

[In considering Volney's results, we must not overlook that they were obtained in glass vessels on a small scale. On the manufacturing scale, and working in iron vessels, higher temperatures cannot be avoided and the formation of nitrous vapours is proportionately increased. The frothing at the last stage of the distillation is generally ascribed to the partial decomposition of sodium bisulphate into pyrosulphate and water: $2NaHSO_4 = Na_2S_2O_7 + H_2O$.]

In a subsequent paper (Journ. Soc. Chem. Ind. 1901, p. 1189) Volney gives the results of working at a much stronger vacuum, viz., 110 mm. absolute pressure. During the first phase, at about 74°, free sulphuric acid acted on the nitrate; during the second phase, at about 85°, the polysulphate did the principal action. The outside temperature rose to 140°. The distilling nitric monohydrate boiled at 30°. With concentrated sulphuric acid there is a great amount of frothing, which does not take place with acid of 60° B. When working with such acid at ordinary pressure, the greatest portion of the nitric acid distils at about 118° without frothing; at a pressure of 110 mm. at 74°, with slight frothing. In both cases the remaining salt-cake consisted of sodium bisulphate and water of crystallization. The nitric acid produced showed in both cases 1·38 spec. grav. at 21° C.; to produce stronger acid, it must be redistilled with concentrated sulphuric acid.

The *condensation* of nitric acid is, properly speaking, only a cooling-process, but it is preferably carried on in such manner that, in the first instance, stronger and weaker acid, coming over at different stages, are separately collected, and that, if possible, the above-mentioned impurities (p. 121) are kept out of the acid and are separately treated. For many years, which now appears strange to us, in this distilling and condensing process only air-cooling was employed, and it is only during the last ten or fifteen years that the much more efficient system of water-cooling, which is so universal in other distilling processes, has been applied for nitric acid, and that with complete success.

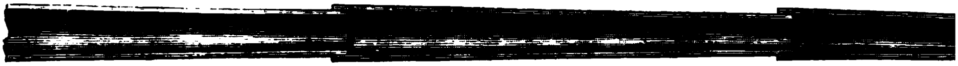
The old condensing-plant for nitric acid consisted entirely of a series of earthenware receivers (Woulfe's bottles), combined in sets of six to twenty and more, according to the size of the retort. Sometimes two or even more of these jars are superposed over one another, in order to increase the cooling-surface. According to the strength of acid intended to be made, they are either left empty or charged with a little water, as already mentioned. Sometimes they are cooled on the outside with water; but generally this is not the case. Each of the jars is provided with a bottom tap for running off the condensed acid; that from the first two receivers is more impure than that of the others, as it contains a little sulphuric acid and iron carried over from the retort. The acid becomes weaker the further the receivers are from the retort. Since the receivers now and then crack with the heat, it is advisable to put them on stoneware saucers provided with a spout, for collecting the acid running out.

The cement used for joining the receivers with the pipes, &c., has been described on p. 120.

This style of condensing-plant is still found at many, especially smaller, works; but it must be considered quite out of date, as its cooling action is too imperfect, as the great number of joints is troublesome to keep tight, as the receivers, on breaking, cause great loss and danger to health and life, and as there is always some loss of uncondensed vapours.

A minor improvement, which can be made, consists in interposing between the retorts and the receivers a somewhat long glass tube, or rather a number of air-cooled glass pipes of slightly conical shape, as shown in fig. 25, with sufficient fall for the condensed acids not to stop in the tubes and run out of the joints.

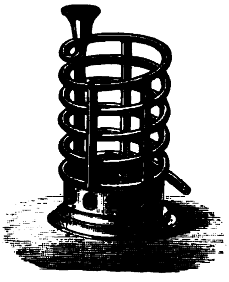
Fig. 25.



With a length of from 10 to 13 feet (the longer the better) the cooling by air is already very efficient. The single tubes are put loosely together, without any cement.

Göbel proposed (Dingl. Journ. ccxx. p. 241), to my knowledge for the first time, the system of cooling such pipes by *water*, employing a long glass tube placed in a trough. This plan must have led to frequent breakages and was probably soon abandoned for that reason, but in principle it was perfectly correct.

Fig. 26.



Much more durable, as well as efficient, are water-cooled *stoneware cooling-worms*, which do away with the necessity of employing a large number of receivers. These coils or worms were first manufactured by Messrs. Doulton & Watts, of Lambeth, as shown in fig. 26, but are now made by many other English and German firms, in various shapes, and are comparatively very durable; good worms stand 300 operations and upwards. They admit of fractionating the products, but are mostly employed when acid of medium strength (up to 82° Tw.) is to be made.

It is nowadays considered indispensable to employ some contrivance for depriving the gas issuing from the condensers of not condensable oxides (NO_2 and NO). Where the acid is made at a sulphuric-acid factory, we may employ a small Gay-Lussac absorbing-tower, consisting of a stack of stoneware pipes filled with coke and continually fed with sulphuric acid of 144° to 152° Tw. The gas enters at the bottom and issues at the top, and thereby gives up all its nitrous and hyponitric acid to the vitriol, which arrives at the bottom as a more or less rich "nitrous vitriol," and can be employed in the manufacture of sulphuric acid. For a ton of nitre from 3½ to 4 cwt. of vitriol are required; and nitrogen acids corresponding to 3 to 5 per cent. of nitric acid

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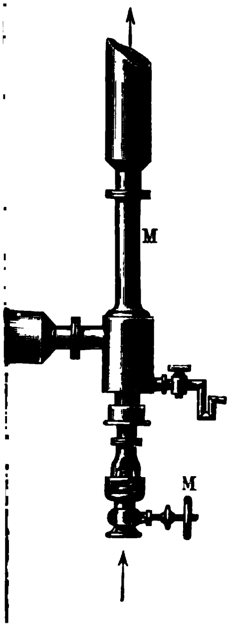
I. *Sulphuric Acid.*



of 1·33 spec. grav. are absorbed by the same, more or less, according to the percentage of chlorides in the nitre.

For such manufactures of nitric acid as are not in connexion with sulphuric-acid works, the coke-tower can be fed with water. If care is taken that an excess of air is always present, not merely the last remnant of nitric acid is condensed, but the lower nitrogen oxides are likewise converted into nitric acid and thus saved.

Far preferable to coke-towers for both the just-mentioned purposes are the "plate-towers" constructed by the Author, in conjunction with L. Rohrmann, and frequently called "Lunge towers." These will be described in detail further on (in Chapter VI.); in this place we will only point out that the use of coke is irrational, because it destroys nitric acid, converting it into nitrous acids and lower oxides. The plate-towers, of which hundreds are in use at nitric-acid works, explosive works, &c., for the above-mentioned purpose, are made of the best fire- and acid-resisting stoneware, and, as will be seen hereafter, they are so constructed as to offer the most intimate possible contact between the gases and liquids. Fig. 27 shows the arrangement as supplied by the Krauschwitzer Thonwaarenfabrik near Muskau, Germany, for the condensation of the last fumes, or the recovery of nitric acid from lower oxides. A B C is the stoneware shell of the tower, D the cover with distributing arrangement, E the plates, F the annular bearers, G drawing-off tap with hydraulic lute, H exit-tube, J sight for observing the condensation, K receiver, M injector for drawing air through the neck N, in connexion with the last receiver O.

Figs. 28 & 29 show how a cooling-worm can be combined with other pieces to form a complete condensing-apparatus. The vapours, coming from two retorts charged with 6 cwt. of nitrate of soda each, first pass through receivers *a a* for impure acid carried over, which is run off into the carboy *b*, then through the cooling-worms *c c*, discharging their contents of pure acid into carboys *d d*, then into a collecting-receiver *e* and into a "plate-tower" *f* for recovering nitric acid from N_2O_4, and finally into a last receiver *g* and injector *h*. The pots *i i*, equally discharging their vapours into *e*, serve for refining (bleaching) the yellow nitric acid (see below).

Such apparatus is especially needed for recovering large quantities of nitrogen oxides, given off in the treatment of waste

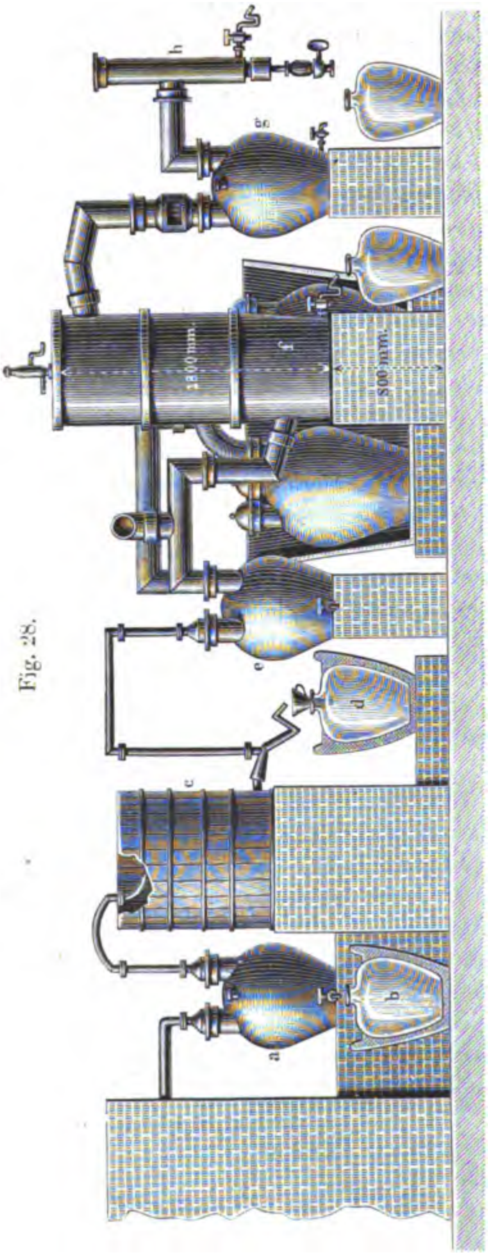


Fig. 28.

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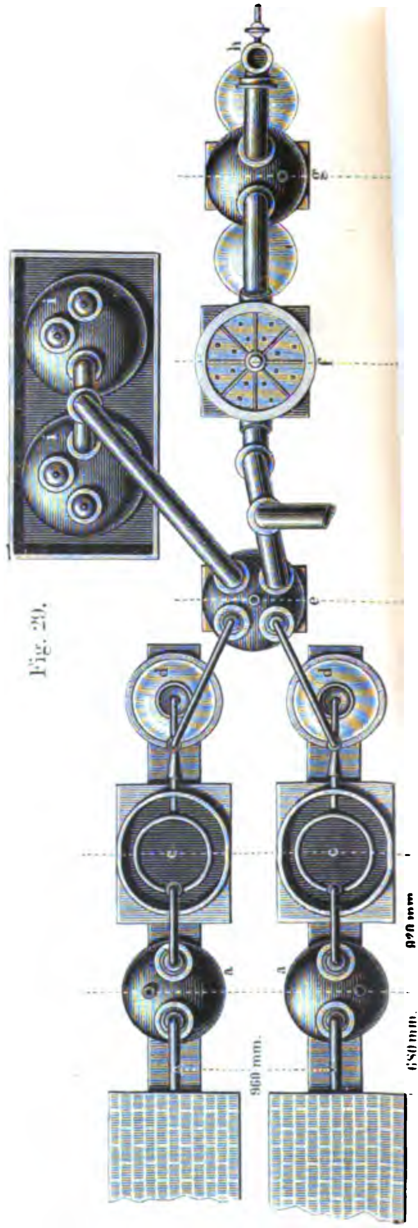

Fig. 29.

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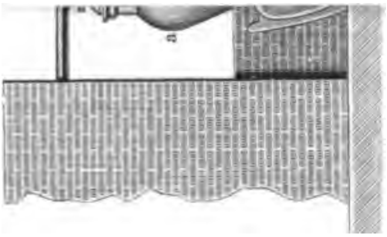
condensing in receiver *b* is run into V_3 or V_4, according to its strength, that condensing in receiver *g* always into V_4.

The *refining* or *bleaching* of nitric acid consists in driving off the lower oxides, so that the acid becomes colourless. This can be done by long heating in a water-bath, which is a tedious operation—much more quickly if a current of air is blown through the gently heated acid ; the air along with the gas contained in it is conducted through a small coke-tower, or, preferably, a small "plate-tower" (see above), fed with water, where dilute nitric



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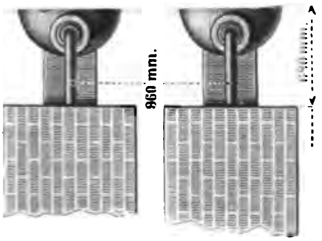

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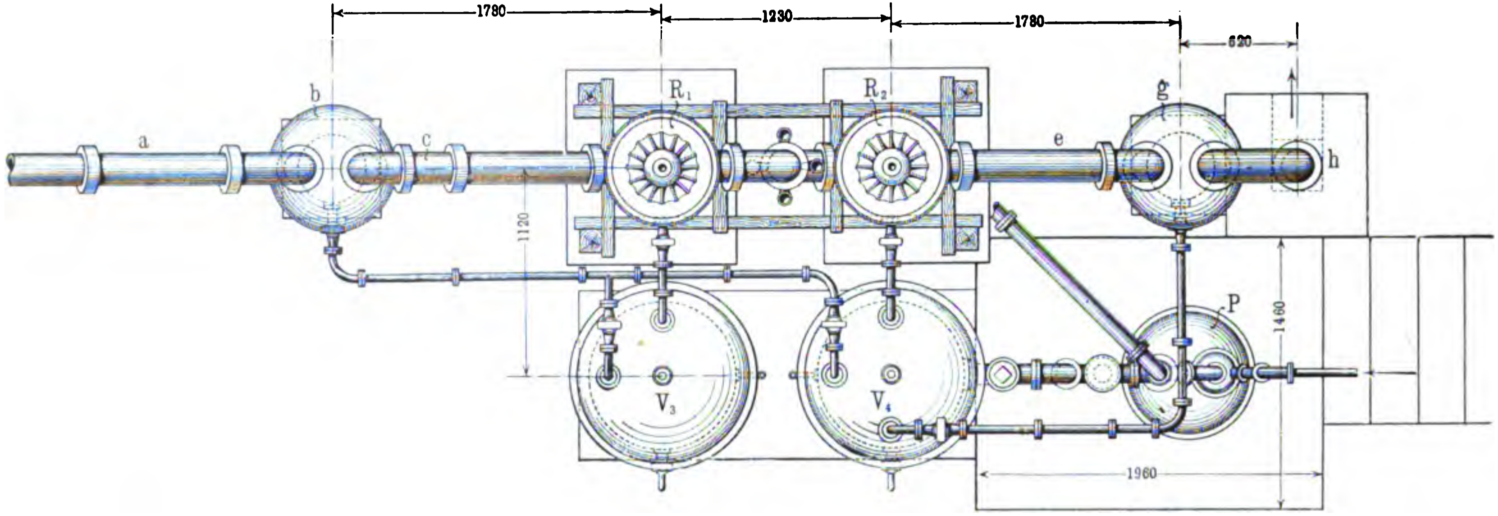
nitrating acids from the manufacture of nitroglycerine, nitrocellulose, aniline, &c., and reconverting them into nitric acid.

For such purposes it is sometimes necessary to combine several plate-towers in sets, one tower being placed higher than the others and delivering its weak acid to those lower ones, to be got up to strength (Rohrmann & Niedenführ, E. P. 29746, 1897).

The weak acid can also be pumped back to be used over and over again, till it has got up to the maximum strength (1·38 or 1·40 spec. grav.). Figs. 30 and 31 show a complete nitric-acid regeneration plant, as employed after long experience by H. H. Niedenführ. Pipe *a* (6 inches wide) comes from the denitrator; it is preferably rather long, say 40 feet, so as to cool the gases which pass through receiver *b* into the first tower R_1; glass tube *c* admits of watching the process. R_1 is filled with 34 Lunge plates. The second tower R_2 contains 30 Lunge plates and above them 2 feet of stoneware balls. The connecting-pipe between the towers contains a "Kirchhoff pipe" *d*, which admits of mixing air with the gases in case of need. Pipe *e* takes the gases away from R_2, through the regulating "sight" *f* into receiver *g*, and through *h* into the chimney. V_1, V_2 are cisterns for feeding the towers; V_1 in the beginning receives a little water, V_2 is entirely filled with water. As soon as the denitrator has been started, water is run down from V_1 into R_1 drop by drop, and from V_2 into R_2 in a strong jet, sufficient for absorbing all nitrous products. The liquid from R_2 is collected in V_4, and is pumped back by the "Plath" pump P (to be described later on) into V_1 and V_2. With this weak acid R_1 is later on fed to such an extent that the acid recovered here comes out with the desired strength and runs into V_3. On the other hand, R_2 is always fed up to the extent of completely recovering the last traces of nitric acid. If the weak acid from V_4 does not suffice for that purpose, it is made up with water, preferably at a temperature of 50° C. The acid condensing in receiver *b* is run into V_3 or V_4, according to its strength, that condensing in receiver *g* always into V_4.

The *refining* or *bleaching* of nitric acid consists in driving off the lower oxides, so that the acid becomes colourless. This can be done by long heating in a water-bath, which is a tedious operation—much more quickly if a current of air is blown through the gently heated acid; the air along with the gas contained in it is conducted through a small coke-tower, or, preferably, a small "plate-tower" (see above), fed with water, where dilute nitric

Fig. 31.



acid is contained. This refining is, of course, unnecessary for nitric acid used in the manufacture of sulphuric acid.

Hirsch (G. P. 46,096) runs the impure acid through a stoneware worm, placed in water of 80° C. Air is blown in at the bottom, and the feed of nitric acid is so regulated that it runs out at the bottom at a temperature of 60° C. and sufficiently bleached. It runs through a second worm placed in cold water, and can then be put into the carboys. The nitrous gases escaping at the top are treated in the usual manner. One worm can purify several tons of acid per diem. The same process may also serve for treating the waste acid of nitroglycerine and nitrobenzene works; in this case air heated to 150° C. or steam is blown in at the bottom, and the feed of acid is so regulated that it issues, at a temperature of 140° C., as comparatively pure sulphuric acid.

The French Government gunpowder works have employed such worms for a long time for this purpose. An ordinary size of worm furnishes 2 cwt. acid per hour, with less than 0·3 per cent. N_2O_4 and practically free from chlorine.

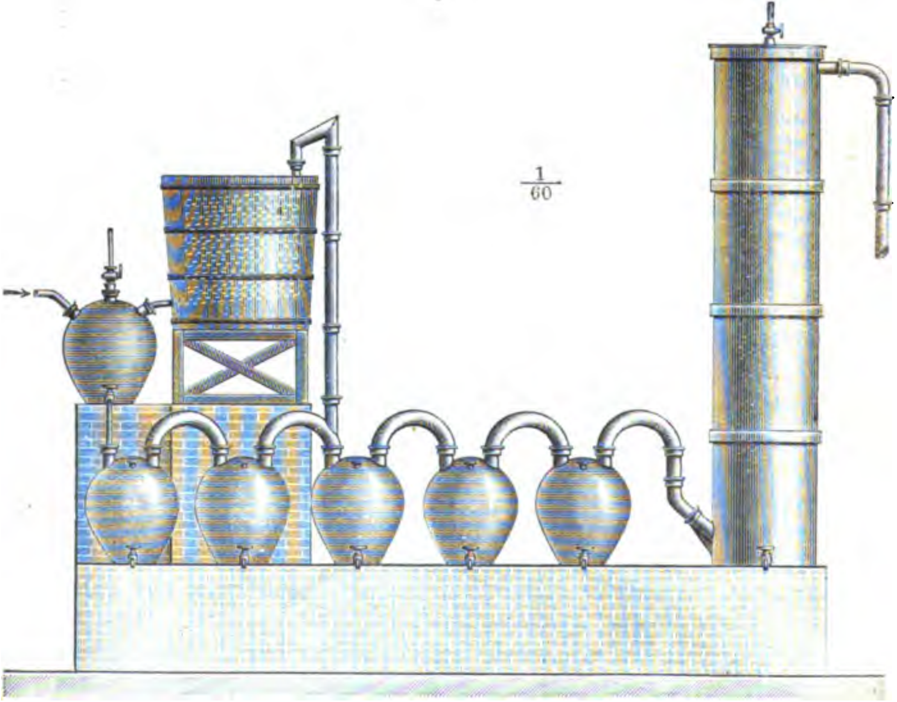
The *Griesheim process* does away with the necessity of bleaching the nitric acid, as it is produced at once in a pure state. (A similar result is aimed at by the apparatus of Guttmann in its recent form and by that of Valentiner, to be described later on.)

The Chemische Fabrik Griesheim (Germ. pat. 59,099) places behind the retort a reflux-cooler, consisting of a Rohrmann stoneware worm contained in a water-tub kept at about 60° C. by the heat of the operation itself. The acid vapours ascending in this cooler are partially condensed there; in consequence of the high temperature the lower nitrogen oxides (together with the chlorine) escape in the state of vapour, and are condensed by air and water in a "Lunge tower" (plate-column) to weak nitric acid. The acid condensing in the worm flows into a receiver, kept at 80° C., and is therefore perfectly pure, no "bleaching" being required. Air is advantageously introduced into the receiver.

This system is illustrated in fig. 32. We notice that the receiver, into which the acid flows back from the reflux-cooler, is provided with a glass pipe reaching down to the bottom, through which air is introduced, which aids in driving off N_2O_4 and chlorine, &c., and also somewhat cools the acid. The strong and pure acid from this receiver is from time to time run off into a lower receiver, not shown in the figure, where it cools down sufficiently for being withdrawn into carboys; the vapours rising here are also passed into the condensing-apparatus. The vapours issuing from the top of the worm are passed through a few receivers and ultimately into the plate-tower.

In practice the temperature of the water in the worm-tub rises to 40° or 50° C. in the case of slow distillation, and 60° in that of rapid distillation; there is always some fresh water run in, care being taken not to cool too much.

Fig. 32.



This apparatus is generally combined with the retorts shown on p. 107. Each charge of 400 kil. nitrate of soda (undried) with 450 kil. sulphuric acid (95 per cent. H_2SO_4) yields first two litres of impure acid, which is run off separately, then 240 or 250 kil. acid of 48° Baumé =91 per cent. HNO_3, with less than 1 per cent. N_2O_4, usually only 0·5 per cent. N_2O_4, and no chlorine at all; then 60 or 65 kil. acid of 42° to 44° Baumé, perfectly clear, and 8 kils. of 25° to 30° Baumé impure acid from the tower.

When working with dried nitrate, the first 250 kil. of acid show 49° B.=93 per cent. NHO_3. The weaker acid (42° B.) can be put back into the retort and recovered as strong acid in the next distillation. The nitre-cake tests about 30 per cent. "free" SO_3.

The Griesheim system has been working for many years at a number of factories with perfect satisfaction.

The same principle as that followed in the Griesheim condensing-plant is the foundation of the patents of Skoglund (G. P. 104,357 and 105,704), where first strong acid is condensed in a stoneware apparatus and the weak, impure acid in a lead condenser [?]. Platt (E. P. 9133, 1901) describes an improvement of the same system.

G. Guttmann (E. P. 8915, 1890) has constructed a nitric-acid condensing-apparatus on the principle of building it up entirely of perpendicular pipes, so arranged that the gases travel upwards and downwards and the acid is run off at the bottom, as it is liquefied, by means of hydraulically sealed branch-pipes, into a common reservoir. The pipes are 8 feet long and have thin walls ($\frac{1}{3}$ inch thick); they perform the condensation incomparably better than ordinary receivers, even when merely cooled by air, but in this case there must be a considerable number of such 8-feet pipes, say 15 or 20, to finish off a charge of 12 cwt. in a shift of 10 or 11 hours. The last pipe is connected with a "Lunge tower" (plate-tower, comp. p. 125), fed with water, in order to retain the uncondensed oxides, in the shape of weak nitric acid, amounting to about 5 to 7 per cent. of the total acid. The Guttmann system is especially suitable for the manufacture of strong nitric acid, of course by means of dried nitrate and strong sulphuric acid.

The former shape of Guttmann's system is shown in our second edition, pp. 890 and 891. Many plants have been erected on that principle with great success. Later on, Guttmann improved his system in various ways. He fixed an injector, fed with compressed air, immediately behind the exit-tube from the still, where the whole of the vapours are still uncondensed. They are thus rapidly drawn away from the retort and mixed with hot air. It is contended that in this way nitric acid with not more than 0·7 per cent. N_2O_4 and at a concentration of 97 per cent. can be made during the whole of the process. The acid is as nearly colourless as can be desired. [If all the acid is 97 per cent., what becomes of the water contained in the sulphuric acid, unless this is of equal strength? Comp. also Volney, p. 121.]

Another improvement of Guttmann's is the substitution of water-cooling for air-cooling, which admits of a considerable saving in pipes. There are only six of these, one exposed to the air and the other five contained in a water-tank, through the bottom of which they pass water-tight by means of rubber rings. Guttmann states that here all the acid can be obtained with 96 per cent. HNO_3, and slightly over 1 per cent. N_2O_4; this increase of N_2O_4 is caused by the greater rapidity of the cooling, which does not leave so much time for the oxidation of NO_2 by the air. Otherwise the condensing battery is similar to the first, inclusive of the plate-tower.

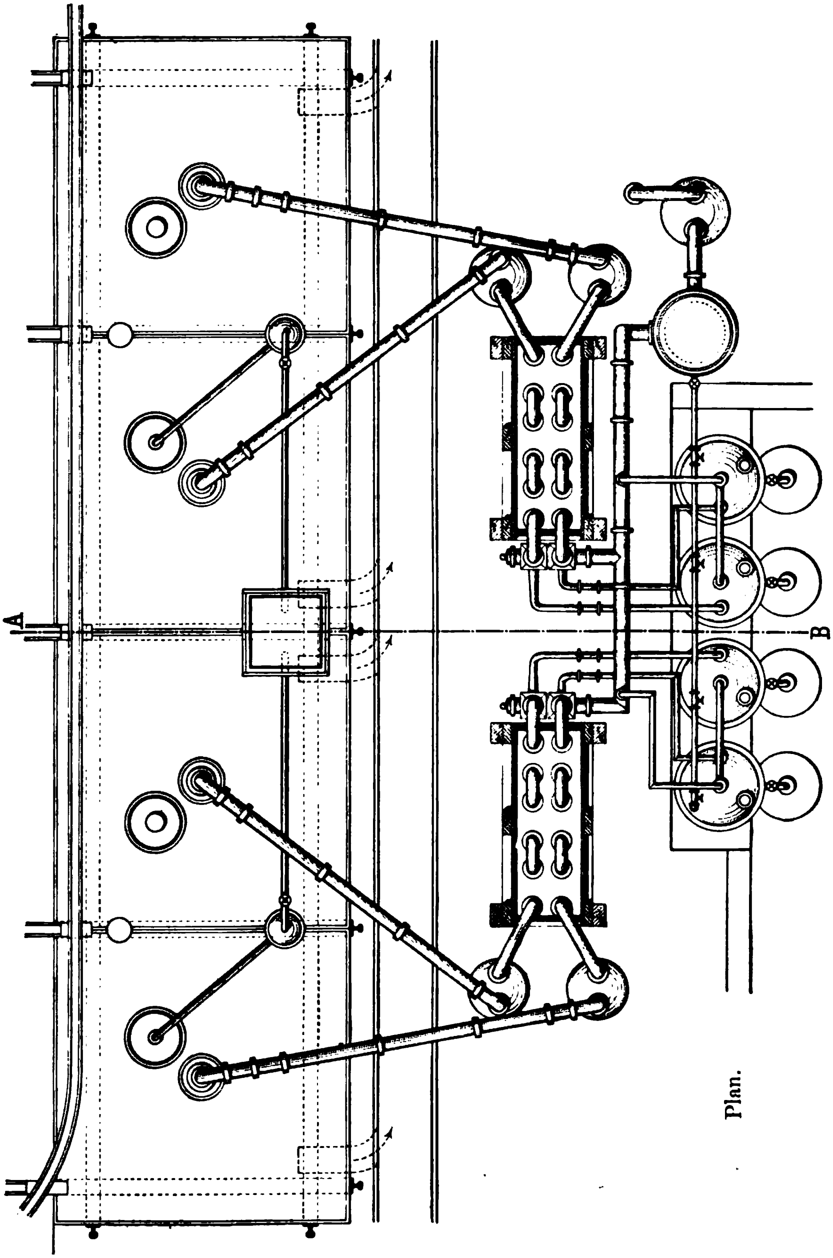
A recent patent of Guttmann's is E. P. 18,189, 1897. In his English patent No. 13,694, of 1901, he describes an arrangement for condensing nitric acid at a comparatively high temperature, when it is less liable to absorb nitrous gases.

Figs. 33, 34, 35 show a Guttmann plant with the most recent improvements, as designed by H. H. Niedenführ and supplied by the Krauschwitz pottery. The drawings are to scale and explain themselves. Each retort, with its set of cooling-pipes &c., decomposes from 12 to 14 cwt. of nitrate of soda in a working day of 12 or 14 hours; with somewhat larger retorts, the cooling-battery can be driven up to 20 cwt. nitrate per day.

Hart (Engl. pat. 17,289, 1894) uses an apparatus consisting of a series of superposed glass tubes, slightly inclined to the horizontal, which starts from an upright stand-pipe and ends in another upright pipe. The pipes are cooled by squirting water upon them or otherwise. The vapours pass simultaneously through all the inclined pipes. As the water squirted on to the glass tubes evaporates, its cooling-action is very strong. Hart asserts that by his method the distillation is effected in half the usual time, with very little fuel and slight formation of N_2O_4. There are 15 tubes to each condenser, about an inch wide and six feet long, for a retort working off 1000 lbs. of sodium nitrate in 8 hours. This system has been introduced with great success in a number of American and English works.

Dieterle and Rohrmann (G. P. 85,240) promote the evolution of gases in the nitric-acid retort by the introduction of some inert gas, which must certainly be an obstacle to condensation. Their object is more rationally attained by the application of a vacuum, as proposed by Valentiner (see also Guttmann's injectors, p. 131).

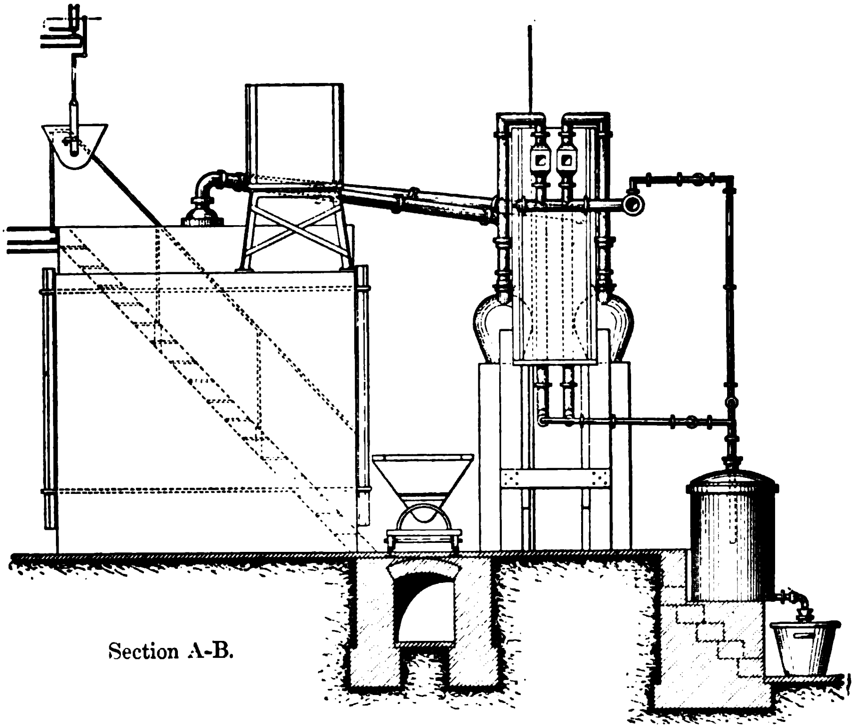
Fig. 33.



Plan.

Valentiner (Eng. pat. 610, 1892, and 19,192, 1895; figs. 36 and 37) manufactures nitric acid in a *vacuum*. The retort in which the sodium nitrate is decomposed with sulphuric acid is connected with a cooling-worm, and this is connected with a receiver, from which, with the interposition of a Woulfe's bottle, the air is aspirated by an air-pump. In this way the most highly concentrated pure nitric acid can be obtained. Perfectly pure nitric monohydrate, produced by this process, is now found in commerce.

Fig. 34.



[Before Valentiner (whose patent dates Sept. 8, 1891), I had shown that this can be done by distilling *in vacuo*, Zsch. f. angew. Ch. 1891, p. 167, published March 15, 1891.]

Hallwell (Chem. Zeit. 1895, p. 118) gives some details of the practical application of Valentiner's process. The cast-iron retort holds 16 cwt. of nitrate of soda and is nearly globular in form (it is shown in fig. 18, p. 112). It is not heated directly by the

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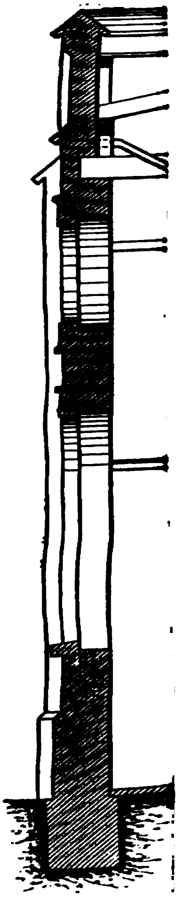

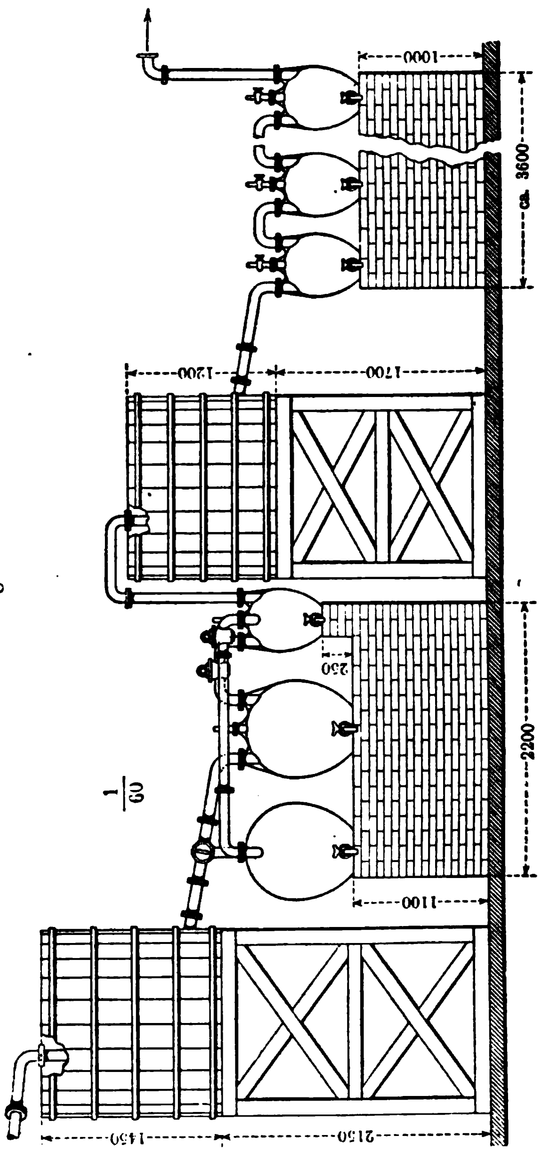
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Fig. 36.

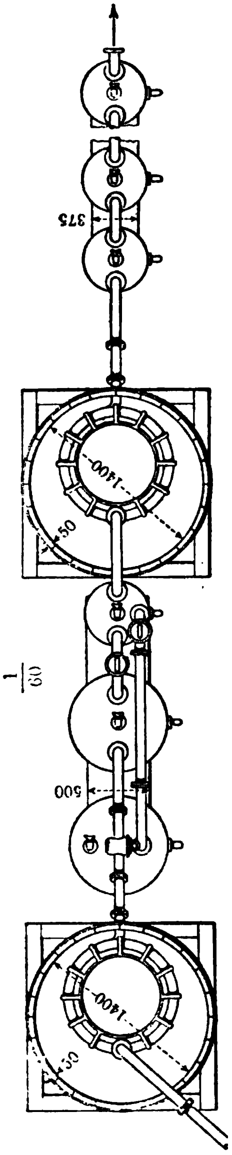
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Fig. 37.

flame, but is surrounded by hot gases. At the top there are necks for the acid vapour, for charging the nitrate, for letting in air, for a thermometer (in a pipe closed at the bottom), and for introducing sulphuric acid. The 8-inch wide neck which carries away the acid vapours is continued into a glass cylinder, through which the inside can be observed, then into an earthenware bend, connected with an earthenware worm of 2½-inch bore and 50 square feet cooling-surface, ending in a three-way cock. Then follow two earthenware receivers of 60 gallons capacity each, with outlet-cocks at the bottom, a receiver of 18 gallons, a smaller earthenware worm (2½-inch bore and 25 square feet cooling-surface), a 60-gallon receiver and five 18-gallon receivers, all of which are provided with outlet-cocks at the bottom and air-cocks at the top. The second small receiver behind the second worm is charged with water, the fourth with sulphuric acid; in these the inlet-pipes are deep enough to dip into the liquid. The last receiver is connected with the air-pump. The two large receivers behind the first worm take most of the condensed acid and are alternately put into series by means of the three-way cock; thus the acid can be drawn off without interrupting the work. The joints are all made by means of flanges provided with rills and a cement made of silicate of soda and asbestos (comp. p. 120). The vacuum helps to keep the joints tight, and they stand very well.

When the nitrate has been charged, all necks are closed, the air-pump is started, and by opening a tap in the connecting-pipe sulphuric acid is drawn in from a store-tank. Much gas is given off at once; first of all nitrosyl chloride, which mostly travels as far as the receivers behind the second worm. When the vacuum has gone up to 500 millimetres of mercury, the fire is started and the thermometer rises to 80°, which temperature is kept up during the principal phase. The vacuum is kept at 650 or 670 millim. In the end the temperature must be raised to 120° or at most 130°. When no more acid distils over, the air-pump is stopped, and the temperature is raised to 170° or 175°, in order to render the nitre-cake more liquid.

Through this low temperature the decomposition of the nitric acid and the reducing-action of the iron are brought to a minimum. Therefore the yield is almost equal to theory, and that mostly in the shape of strong acid. With undried nitre and sulphuric acid of 142° Tw. the yield, according to Hallwell, is 95·7 per cent. of the theoretical, in the shape of acid of 90½° Tw. (78 per cent. HNO_3), and 3·8 per cent. impure acid of 21½° Tw., together 99·5 per cent. With undried nitrate and sulphuric acid of 160° Tw. the yield is 99 per cent. nitric acid of 93½° Tw. (81 per cent. HNO_3), and 0·8 per cent. as dilute acid, together 99·8 per cent. The weak acid is left in the receivers till it has risen to 66° Tw. With dry nitrate and sulphuric acid 168° Tw., real nitric monohydrate can be obtained. The usual strength, 100° Tw., contains only 0·04 per cent. N_2O_3 and no chlorine at all, against 0·95 to 1·92 per cent. N_2O_3 in the ordinary 100° acid.

Hallwell states that while in other processes charges of 6 to 8 cwt. nitrate require from 15 to 20 hours to be worked off, here a 16 cwt. charge takes only 7 or 8 hours, and two charges are easily made in 24 hours, which means four or five times the usual quantity. The consumption of coal is 8 or 9 parts for firing and 6 or 7 parts for the vacuum, together 14 or 16 parts to 100 nitrate, against 32 to 35 parts in the old process. There is also no steam or compressed air needed for refining the acid. The durability of the retorts is greater than in the old process, and the earthenware vessels do not suffer at all. The temperature of the first receivers is only 35° to 42°, the back receivers are cold; they never crack, nor do they collapse through the atmospheric pressure, as they are made rather thick-walled and nearly globular in shape. Any cracks in the pipes or bad places in the receivers are cured by putting on asbestos paper soaked in silicate of soda solution. If too much frothing is observed through the glass cylinder, this is at once remedied by opening the air-cock. The total length of the apparatus is only 40 feet, the width of the furnace 17 feet, that of the condensing-plant 5 feet. Large apparatus holding from 50 to 60 cwt. is to be constructed. The sanitary drawbacks of the ordinary nitric acid manufacture are absent when working with a vacuum.

The action of the acid gases escaping from the condensation (especially NOCl) upon the air-pump must be prevented by charging the last receiver with milk of lime, which should, of course, be renewed from time to time.

Further communications on the Valentiner process have been made by Franke (Chem. Zeit. 1897, p. 511). For each ton of nitrate decomposed there should be about 87 cubic feet condensing-space. The retorts should be entirely surrounded by the fire, or their upper part and the branch-pipe should be protected by an acid-proof lining. With sufficient condensing-space and good cooling, and if the formation of N_2O_4 is prevented, the yield should be almost the theoretical, since only part of the chlorides can escape. The nitre-cake is free from nitrogen compounds, and the first receiver, which is filled with water, is not changed even after several operations. The temperature during the distillation itself is hardly 100° C., but later on it must rise to 175°, to make the nitre-cake sufficiently liquid. The hot vapours then formed may decompose some of the condensed acid, unless they are very well cooled immediately behind the retort. Theoretically 1000 kil. 96 per cent. nitrate of soda, with 2 per cent. water, treated with 1000 kil. 94 per cent. sulphuric acid, should furnish 796·5 kil. nitric acid of spec. grav. 1·486 (89·3 per cent. HNO_3); from 1000 kil. 96 per cent. nitrate, previously dried, 771·5 kil. nitric acid spec. grav. 1·497 (92·2 per cent. HNO_3) should be obtained, and practically the yield need not be much less. But with concentrated acid there is much frothing, through the production of N_2O_4, because the acid does not at once penetrate through the nitrate; this is avoided by employing more sulphuric acid, or by introducing liquid nitric acid into the retort. Valentiner has recently recommended the preparation of stronger nitric acid by redistilling the weak acid in the vacuum with concentrated sulphuric acid; but this double distillation costs decidedly more acid, coals, and wages in comparison with the direct distillation. Comp. also the same author in Zsch. angew. Ch. 1899, p. 269. Bergmann (ibid. 1900, p. 1003) also reports favourably on this process, but finds it necessary to pass the gases through milk of lime before they reach the pump, in order to retain the nitrosyl chloride. He consumes 5 cwt. coals for a charge of 16 cwt. nitrate.

The manufacture of nitric acid by means of a vacuum has also been patented by Dreyfus (E. P. 13,826, 1895), who mentions a temperature of 170°–190°.

In spite of the disadvantage that a double distillation is required in order to obtain very strong nitric acid, the Valentiner system has been introduced in many factories. Owing to the low temperature, the material of the apparatus is more durable, the product is pure, and the yield almost equal to theory. In the latter respect, as Guttmann remarks, the results in all well-conducted factories are about the same. 100 parts real $NaNO_3$ ought to yield 74·13 parts real HNO_3; but of course any NO_2 contained in the acid must be deducted from this, and at least 5 per cent. is necessarily obtained as weak acid (tower acid).

The Valentiner system has been represented as decidedly inferior to Guttmann's by some observations made in a scientific publication in 1901, but has been quite as strongly defended from the other side. We can here only give the respective references: Zsch. für angew. Chemie, 1901, pp. 413, 495, 571, 658, and 731.

Compare also Volney's results on the smaller scale when distilling in a vacuum, p. 121.

The principal choice of a condensing system nowadays seems to lie between the systems of Griesheim, Guttmann, and Valentiner. Their results (allowance being made for the exaggerations of interested parties) seem to be so nearly alike, that it becomes very much a question of first cost of the apparatus, which we cannot treat of here, since patent licences play a considerable part in this case.

Concentration of Nitric Acid.—(Comp. Valentiner's process, p. 138). Colin (French pat. 211,045) prepares fuming nitric acid of spec. grav. 1·5 by distilling nitric acid of 1·4 with sulphuric acid of 1·84 in enamelled cast-iron retorts, and employing a glass three-way cock for separating the distillates. [This apparatus does not appear to be practicable.]

Erouard (Germ. pat. 62,714) also concentrates dilute nitric acid, or waste acids from nitrating processes, by adding strong sulphuric acid, or a solution of $CaCl_2$ or $MgCl_2$ [!], and distilling the mixture in a vessel in which it travels in a zigzag direction.

H. A. Frasch (Germ. pat. 82,578) prepares highly concentrated nitric acid by passing the vapours from the nitric-acid retort through a tower heated above the boiling-point of the acid, in which hot concentrated sulphuric acid is descending, or in which other dehydrating substances, such as anhydrous sulphate of soda or burnt plaster-of-Paris, act upon the mixed vapours.

The Verein Chemischer Fabriken in Mannheim (G. P. 85,042) places between the still and the condenser a dephlegmator, from which the dilute acid condensed there runs back into the still. This dephlegmator is kept at a temperature of 85° C., so that the concentrated acid can pass on.

The *fixed residue* from the manufacture of nitric acid (called "*nitre-cake*," or, in the workmen's language, "sally nixon," a corruption of "sal enixum") is practically a mixture of neutral and acid sodium sulphate. It generally contains from 25 to 30 per cent. "free acid" (*i. e.* bisulphate acid) calculated as SO_3, and only traces of nitrate. We shall treat of it in detail in Vol. II., and here only remark that most of it is worked up with common salt into ordinary salt-cake and hydrochloric acid; part of it is also used up directly for glass-making, but no doubt not to great advantage. Kirkman (E. P. 5703, 1889) employs it as an absorbent for ammonia, in which case a profitable utilization of Na_2SO_4 will be very difficult.

Giles, Roberts, and Boake (Engl. pat. 11,979, 1890) convert ordinary nitre-cake by addition of sulphuric acid into "pentasulphate," Na_2O, $5SO_3$, $3H_2O$, which can be packed in iron drums [?] or ordinary casks and usefully employed for certain purposes (comp. Uebel's "polysulphate," p. 117).

The *cost of manufacturing nitric acid* at a Continental factory (some years ago) was as follows, and can be easily reduced to current English prices:—

1. *For acid of* 36° *Baumé* (=sp. gr. 1·334 or 50 per cent. NO_3H).

	£	s.	d.
4 charges of 4 cwt. each nitrate of soda, at 16*s*.	12	16	0
16 cwt. sulphuric acid 144° Tw., at 3*s*.	2	8	0
10 cwt. lignite (very inferior quality), at 9*d*.	0	7	6
2 men, at 3*s*.	0	6	0
Interest and writing off the plant	0	8	0
General expenses	0	1	6
Packages, &c.	1	16	0
Yield: 21 cwt. acid at 36° Baumé	19	3	0
Cost of 1 cwt. acid at 36° Baumé	0	18	3

2. *For acid of* 50° *Baumé* (=sp. gr. 1·532=93 per cent. NO_3H).

	£	s.	d.
6 cwt. of nitrate of soda (dry), at 19*s*.	5	14	0
6 cwt. sulphuric acid 168° Tw., at 5*s*. 6*d*.	1	13	0
6 cwt. lignite, at 9*d*.	0	4	6
Wages—2 men	0	6	0
Sundries and general expenses	0	12	0
Small stores	0	11	0
Yield: 3 cwt. 2 qrs. 10 lb. acid	9	0	6
Deduct value of 5 cwt. nitre-cake	0	15	0
	8	5	6
Cost of 1 cwt. of acid 50° Baumé	2	6	0

The cost price at a French works is stated by Sorel, for 100 kil. of acid of 36° Baumé, made in large cylinders :—

	francs.
Supervision (¼ of the foreman's wages)	0·59
Wages of workmen	1·13
76·33 kil. nitre at 27 frs.	20·69
83·95 kil. acid 60° B. at 2·25 frs.	1·89
36 kil. coal at 2·15 frs.	0·77
Lighting	0·27
Repairs	2·55
General expenses	0·65
	28·54
Deduct 88·54 kil. nitre-cake at 2·25 frs.	1·99
Cost of 100 kil. nitric acid 36° B.	26·55

Utilization of waste acids from nitrating processes.—Enormous quantities of nitric acid, always mixed with strong sulphuric acid, are consumed in the manufacture of nitrobenzene, nitrotoluene, and other aromatic compounds required in the manufacture of colouring-matters, as well as in that of nitroglycerine, nitrocellulose, and other substances serving as explosives. The waste acids formed in the first class of processes contain but little nitric acid, generally only about 1 per cent., with about ¼ per cent. of nitrobenzene &c. They may be used directly in the Glover tower, where the nitric acid is utilized as well as the sulphuric acid. Special processes for denitrating these acids are rarely employed, least of all with a view of recovering the nitric acid, which does not pay for the trouble and expense.

The case is entirely different with the waste acids from the manufacture of explosives. These contain much more nitric acid than those from the manufacture of nitrobenzene. Nitroglycerine waste acid contains about 10 per cent. HNO_3, 70 H_2SO_4, 20 H_2O; gun-cotton acid 11 or 12 HNO_3, 80 H_2SO_4, 8 H_2O. These acids, if it is not possible to consume them in a Glover tower, can be used for replacing part of the sulphuric acid in the nitric-acid manufacture; or else they are denitrated by steam, producing dilute sulphuric acid (which is concentrated by evaporation and used over again) and nitric acid, together with lower nitrogen oxides. By passing the vapours mixed with air through some receivers and then through a "Lunge tower," the nitrogen oxides are also converted into nitric acid, the total being recovered as nitric acid of 70° or even 80° Tw. (comp. pp. 125 & 127).

A detailed description of the denitrating process is found in O. Guttmann's 'Manufacture of Explosives' (London, 1895), vol. ii. p. 177.

The denitration is altogether similar in this case to the process to be described in Chapter VI. in connection with the recovery of nitre in the lead-chamber process. The best kind of apparatus is a column of Volvic lava, made in one piece and packed with bits of flint or quartz. Steam is injected to such an extent that the outflowing denitrated sulphuric acid has a specific gravity of about 1·635; it is often strongly coloured. The vapours are passed, together with air, injected or aspirated by suction, through a number of receivers, say 6 or 8, or else a small Guttmann battery, and then into a Lunge tower fed with a very thin stream of water, followed again by a few receivers.

Where very large quantities of nitrous vapours have to be regenerated, whether it be from waste acids of the just-mentioned kind or from other chemical processes, it is best to combine several plate-towers, one of which may be placed above the others so as to feed them with the weak acid produced therein. Thus all the recovered nitric acid can be brought up to spec. grav. 1·38. The Krauschwitzer Thonwaarenfabrik, Muskau (Silesia), furnishes this kind of plant. A very complete apparatus for this purpose has been arranged by Niedenführ, as described and illustrated *supra*, p. 127.

Where sulphuric anhydride is made, these waste acids can be brought up to strength by means of SO_3 and used over again.

Various Processes for the Manufacture of Nitric Acid.

Glock (G. P. 110,254) heats nitrate in a pan provided with stirring-gear to 120°–150° and runs in the equivalent quantity of sulphuric acid, previously heated to 100°–130°, in a thin jet. The end of the decomposition is facilitated by steam or a thin jet of water. At last air is blown through, whereupon the solid, pulverulent neutral sodium sulphate is ladled out. Or else the nitrate is from the first heated to 250° C. [This process looks extremely impracticable.]

Manufacture of Nitric Acid without Sulphuric Acid.—Campbell & Walker (E. P. 9782, 1894) grind nitre-cake with nitrate of soda and charge the mixture into retorts provided with a mechanical agitator.

Garroway (E. P. 6777, 1899; Journ. Soc. Chem. Ind. 1901, p. 1191) mixes ordinary acid nitre-cake with sodium nitrate, heats the mixture in a retort, and blows a spray of weak nitric acid by means of compressed air over the mixture. The nitrogen oxides, mixed with steam and air, are regenerated by condensing-tubes and towers into nitric acid (see pp. 125 & 127). It is alleged that ultimately a 96-per-cent. acid can be produced [? this certainly cannot be done by any ordinary regenerating process]. The residue is neutral salt-cake, testing 98·36 per cent. This process is stated to have been worked for three years at Glasgow.

Garroway (E. P. 2466, 1895) also prepares nitric acid by heating a mixture of nitrate of soda and ferrous sulphate or alum, obtaining sulphate of soda and oxide of iron or alumina. He also patents the decomposition of sodium nitrate by silica (E. P. 2489, 1896).

Very interesting are the processes intended for decomposing nitrate of soda in such manner that, besides nitric acid, caustic soda is formed. Theoretically these processes are enormously superior to the ordinary process; there is no waste of sulphuric acid and no production of nitre-cake, which is a product of very low value, but the soda is brought into its most valuable form, as caustic or carbonate. But not one of these processes has come into regular use. They all suffer from the drawback that the temperature of decomposition is too high, which necessitates special shapes of retorts and great wear and tear of these, and that some of the nitric acid (often a very considerable proportion) is reduced to lower oxides. These can be reconverted into nitric acid by means of intimate contact with air or water, in "plate-columns" (Lunge towers) or otherwise; but this cannot be done without a perceptible loss, and it never leads to the production of very strong nitric acid, such as is required for the manufacture of explosives and many other purposes.

We therefore only refer to the enumeration of these processes in vol. iii. (2nd edition) p. 254 *et seq.*, and briefly quote the more recent additions to the subject.

A special retort for the Lunge and Lyte process (decomposition of $NaNO_3$ by Fe_2O_3) has been constructed and patented (G. P. 90,654). It consists of a revolving cylinder placed in a sloping position, with inner projections and contrivances for feeding and exhausting without stopping the process. A full description of the whole process has been given by J. L. F. Vogel in the Eng. & Min. Journ. 1900, p. 408.

Main, Stevenston, and McDonald (E. P. 23,819, 1895) heat sodium nitrate with manganese oxides. Garroway (G. P. 79,699) employs lime and superheated steam. Vogt (E. P. 22,018, 1891) heats with lime, ferric or manganese oxides in a current of superheated steam and carbon dioxide.

Darling and Forrest (E. P. 5808, 1894) propose obtaining nitric acid by the *electrolysis* of fused alkaline nitrates, together with metallic potassium or sodium. Patent no. 13,171, 1895, extends this process to the production of nitrous fumes (together with sodium oxide) for the manufacture of sulphuric acid.

Siemens and Halske (Germ. pat. 15,103) suggest utilizing the well-known formation of nitric acid by the direct union of oxygen and nitrogen under the influence of the silent electrical discharge. This reaction, which under ordinary circumstances is much too slow, is to be promoted by adding ammonia-gas, which causes an abundant formation and separation of solid ammonium nitrate.

McDougall also employs electricity (E. P. 4643, 1899).

Crookes (Elect. World, xxxiii. p. 319; Fischer's Jahresb. 1898, p. 307) shows that by means of induction-sparks 74 grams $NaNO_3$ are formed by one kilowatt-hour, or 1 ton of nitrate by 14,000 kilowatt-hours. This would at present cost £25 with the best steam-engines and dynamos working day and night, and is therefore out of the question, but it might be done by very cheap water-power.

W. Ostwald (B. P. no. 898, 1902) improves the well-known formation of nitric acid from *ammonia*, under the influence of platinum, by passing that gas, with more or less its volume of atmospheric air, at a red-heat over smooth platinum, coated with a layer of spongy or black platinum. The smooth platinum causes the ammonia to be burnt into nitric acid, with practically no formation of free nitrogen. The finely divided platinum accelerates both reactions, the second one more than the first. By moderate use of the finely divided platinum with the smooth platinum, the operation can be so performed that the reaction takes place rapidly, but without any great formation of free nitrogen. The same effect is produced by iridium, rhodium, palladium, the peroxides of lead and manganese, the oxides of silver, copper, iron chromium, nickel, and cobalt.

Statistics concerning nitric acid are very difficult to obtain. For the year 1894 the well-known firm Gehe & Co., of Dresden, reckon that the production of nitric acid in Germany was 54,000 tons, for which 40,000 tons nitrate of soda were consumed. In the United States, in 1900, 27,890 tons nitric acid of various strengths were made (U.S. Census Bulletin, No. 210).

Transportation of Nitric Acid.—Nitric acid is usually sent out in glass carboys or earthenware jars. Strong acid, when kept in tightly closed vessels, may give off a dangerous amount of vapours, especially in the sunshine or under similar conditions. Guttmann recommends covering the carboys loosely with earthenware or glass cups fitting over the necks, also making the straw in which the carboys are packed incombustible by dipping it in a solution of zinc chloride or nitre-cake [which will very quickly corrode it; neutral sodium sulphate is decidedly preferable!], and to lime-wash the top of the carboys exposed to sunlight; also to store the carboys in an excavated chamber, where a breakage will not cause much damage, as the place can be swamped with water. Sometimes fires are caused by nitric acid from a broken carboy inflaming the straw; in which case the poisonous vapours are exceedingly dangerous to inhale (comp. Chap. VI.).

Strong nitric acid can be kept and treated in cast-iron or wrought-iron or leaden vessels, but, of course, any dilution caused by the moisture of air or otherwise will cause a violent action. Aluminium resists nitric acid even in a somewhat more dilute state.

Protection against accidents caused by fumes of Nitric and Nitrous Acid.—In the sixth Chapter we shall treat of this subject in connection with Gay-Lussac and Glover towers. I will here only allude to the official rules published by the "Berufsgenossenschaft für chemische Industrie," Fischer's Jahresb. 1899, p. 411, and the report by Duisberg, Zsch. f. angew. Ch. 1897, p. 492.

Pumping of Nitric Acid.—For this purpose Paul Kestner, of

Fig. 38.

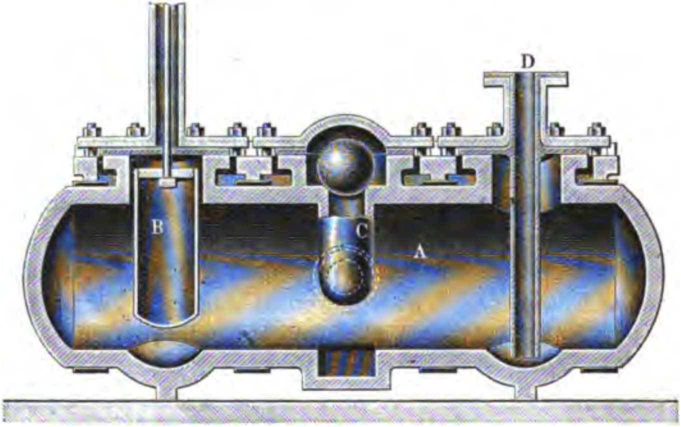
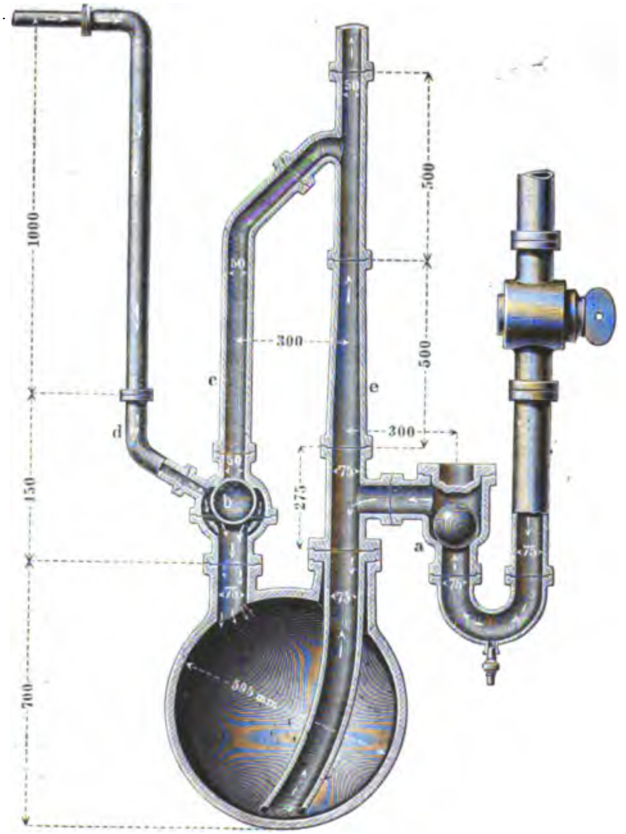

D
B
C
A

Fig. 39.


1000
50
500
50
300
c
e
500
d
300
50
275
75
150
b
a
75
75
75
75
595 mm.
700

Lille, has constructed special "pulsometers" entirely of stoneware, one form of which is shown in fig. 38—exhibiting the cylinder A, the float B, the air-valve C, and the delivery-pipe D. All flanges are made tight by thin sheet asbestos, the faces being ground and polished. The working of this "pulsometer" is exactly like that of the cast-iron pulsometer described in Chap. VI.

Another automatic and continuous pulsometer has been constructed by Plath, and is sold by the Vereinigte Thonwaarenwerke, Charlottenburg (fig. 39). It also consists entirely of stoneware, including the valves. The acid enters through valve *a*, the hollow ball of which is weighted so that it just sinks in the liquid, and is therefore easily raised by the inflowing liquid. When the vessel is full, the acid gets up to the other valve, the ball of which, *b*, is so light that it even floats upon water. It is, of course, raised by the acid and shuts off the upper air-way *c*. The compressed air now enters through *d* and forces the acid up into the rising-main *e*, and thus into the upper store-tank. As soon as the vessel is empty, the ball *b* descends, being aided by the short column of liquid in *c*. The compressed air cannot now enter the vessel, and, as there is now no counter pressure, the ball *a* is again raised and the acid flows in from the lower tank, the air escaping through *e*. This action continues so long as there is acid in the lower store-tank and compressed air in *d*. Balls *a* and *b* are accurately ground as usual for pumps &c. A new model made by the same firm prevents any escape of compressed air during the charging.

Schärtler (Zsch. angew. Ch. 1901, p. 729) describes apparatus constructed by O. Guttmann from stoneware for the purpose of raising acids, viz., first an injector for working with steam or compressed air, and, secondly, a constantly acting acid-egg.

Analysis of Nitric Acid.—Nitric acid is frequently merely tested by the hydrometer, but this is quite illusory, owing to the influence of the nitrogen peroxide (p. 102). When tested by titration it should be noticed that methyl-orange is destroyed by nitrous acid; but this can be overcome by adding the indicator only towards the end of the titration (comp. Chap. III., where the indicators are more specially treated). When titrating with caustic soda, this indicates all acids: HNO_3, N_2O_4 (which reacts $=HNO_3+HNO_2$), H_2SO_4, &c. At least a permanganate titration should be made as well, in order to estimate N_2O_4.

The *impurities contained in commercial nitric acid* are as follows—*chlorine, sulphuric acid, fixed residue, iron*: all found and estimated by well-known methods. *Nitrous acid or nitrogen tetroxide* is best estimated by means of potassium permanganate, running the acid from a burette into the warm diluted solution of permanganate, as will be described in the next Chapter. (The influence of NO_2H on the specific gravity of nitric acid has been noticed above.) *Iodine* is recognized by boiling 1 c.c. in order to remove the lower nitrogen oxides and to oxidize all iodine into iodic acid, diluting with 5 c.c. previously boiled water, and adding a few drops of a solution of potassium iodide and starch, made with water free from air. A blue colour shows the presence of iodine in the original acid, according to the reaction

$$HIO_3 + 5KI + 2H_2O = 5KOH + 6I.$$

This test, according to Beckurts (Fischer's Jahresb. 1886, p. 305), is much more delicate than the ordinary one of reducing the iodate by zinc and extracting the iodine set free by carbon bisulphide; but Beckurts's test would, of course, lead to serious errors unless a check test was made with the iodide of potassium employed, which might itself contain some iodate.

CHAPTER III.

THE PROPERTIES AND ANALYSIS OF THE TECHNICALLY EMPLOYED OXIDES AND ACIDS OF SULPHUR.

SULPHUR DIOXIDE, SO_2. (Sulphurous Anhydride; erroneously designated Sulphurous Acid.)

SULPHUR dioxide is at the ordinary temperature and pressure a colourless gas of suffocating smell, neither supporting combustion nor combustible itself directly. Even when greatly diluted with air it has a very injurious action upon plants and animals (comp. further on, p. 154).

Sulphur dioxide contains 50 per cent. by weight of sulphur and 50 per cent. oxygen. Its specific gravity has been found by various observers = 2·222 to 2·247 (air = 1); calculated from the molecular weight = 2·216. A litre of the gas at 0° C. and 760 millim. pressure weighs 2·8608 grams. Its coefficient of dilatation is not exactly equal to that of air, but rather larger, especially at lower temperatures, namely for each 1° C., according to Amagat:—

Between	0° and 10°	0·004233
„	10° „ 20°	0·004005
At	50°	0·003846
„	100°	0·003757
„	150°	0·003718
„	200°	0·003695
„	250°	0·003685

Its specific heat, compared with its equal weight of water is = 0·1544; compared with its equal weight of air = 0·3414. Mathias (Compt. Rend. cxix. p. 404) gives it as between −20° and +130° C.:

$$0{\cdot}31712 + 0{\cdot}0003507t + 0{\cdot}000006762t^2.$$

The density of *saturated* vapour of SO_2 (that is, in contact with liquid SO_2) at various temperatures (water of 0° = 1) is, according to Cailletet and Mathias (Compt. Rend. civ. p. 1536):—

At	7·3° C.	... 0·00624	At	100·6° C.	... 0·0786
,,	16·5	... 0·00858	,,	123	... 0·1340
,,	24·7	... 0·0112	,,	130	... 0·1607
,,	37·5	... 0·0169	,,	135	... 0·1888
,,	45·4	.. 0·0218	,,	144	... 0·2195
,,	58·2	... 0·0310	,,	152·5	... 0·3426
,,	78·7	... 0·0464	,,	154·9	... 0·4017
,,	91·0	... 0·0626	,,	156	critical point.

The heat of formation of one molecule of SO_2 (=64) from ordinary (rhombical) sulphur is =71,080 cal. (Thomsen), or 69,260 cal. (Berthelot).

By moderate cooling sulphur dioxide can be condensed to a liquid, even without application of pressure. Liquid SO_2 is a colourless mobile fluid, of about the same refractive power as water, boiling at −10° C.; but on drawing it off at the ordinary temperature from a reservoir it remains liquid for some time, the evaporation cooling it down below its boiling-point. Its latent heat at 0° is 91·2, at 10° 88·7, at 20° 84·7, at 30° 80·5.

Its vapour-tension is:—

At 0° C. = 0·53 atmosphere overpressure.
,, 10° = 1·26 ,, ,,
,, 20° = 2·24 atmospheres ,,
,, 30° = 3·51 ,, ,,
,, 40° = 5·15 ,, ,,

The specific gravity of liquid sulphur dioxide at various temperatures has been accurately determined by A. Lange (Zsch. angew. Ch. 1899, p. 275) as follows:—

Temperature.	Specific gravity.	Temperature.	Specific gravity.
−20° C.	1·4846	+20° C.	1·3831
−10°	1·4601	25°	1·3695
− 5°	1·4476	30°	1·3556
0°	1·4350	35°	1·3441
+ 5°	1·4223	40°	1·3264
10°	1·4095	50°	1·2957
15°	1·3964	60°	1·2633

He found that absolutely anhydrous liquid SO_2 does not act upon iron up to 100° C. Technical sulphur dioxide has a slight action, owing to the presence of a little water. The temperature at which this takes place increases with the purity of the acid, *e.g.* it is 70° with acid containing 0·7 per cent. H_2O. Since liquid SO_2 cannot dissolve more than 1 per cent. water, even the most impure product cannot act on the iron vessels in which it is transported at ordinary temperatures. The mixture of ferrous sulphite and thiosulphate formed acts as a protecting crust. In ice-machines where SO_2 is the active agent, and where the temperature in the pumps may rise considerably, only absolutely anhydrous SO_2 should be employed. (Comp., on this subject, also Zsch. angew. Ch. 1899, pp. 300 & 595.)

Sulphur dioxide is produced by burning brimstone, and by heating (roasting) many metallic sulphides, in the presence of air; by the action of strong mineral acids, both on its own salts, the sulphites, and on the thiosulphates and all polythionic acids; by heating sulphuric anhydride with sulphur, or by heating oil of vitriol with brimstone, coal, organic substances, or several metals; by strongly heating the vapour of sulphuric anhydride, or sulphuric acid, with simultaneous formation of oxygen and water respectively; and by igniting many sulphates, whereby the sulphuric anhydride first liberated at once splits up into sulphur dioxide and oxygen.

Thus sulphur dioxide is produced from sulphuric acid or anhydride in many ways by reductive processes. On the other hand, the sulphur dioxide passes over, even more easily, into sulphuric acid by oxidation processes; and it is accordingly one of the most frequent and potent reducing agents. Under certain conditions, by the action of light, of the electric current, or of a very high temperature and pressure combined, the sulphur dioxide splits up into sulphur and sulphuric anhydride. In the presence of oxygen (for instance, that of atmospheric air), or of bodies easily parting with their oxygen (such as the higher oxides of nitrogen, of manganese, of lead), sulphuric acid or its salts are formed. A very important reaction is that between SO_2 and sulphuretted hydrogen, H_2S. When completely dry the two gases do not seem to act upon each other. Even in the presence of moisture no action takes place if the temperature is above 400° C. (E. Mulder). At the ordinary temperature water and sulphur are produced, but at the same time also pentathionic acid, according to the equation

$$5\ SO_2+5\ H_2S=S_5O_6H_2+4\ H_2O+5\ \dot{S}.$$

This action occurs simultaneously with the simple reaction,

$$SO_2+2\ H_2S=2\ H_2O+S_3,$$

one or the other of these prevailing, according to the proportion of the two gases in the mixture.

With water, sulphur dioxide does not form sulphurous acid proper, SO_3H_2, but only, under certain conditions, a solid compound with much more water (9, 11, or 15 H_2O to SO_2), which has not yet been definitively investigated. Sulphur dioxide dissolves pretty freely in water; and this solution behaves in every way as if it contained the real acid SO_3H_2; but constantly, even at the ordinary temperature, the dioxide (SO_2) evaporates from it. One volume of water absorbs, under 760 millim. pressure and at 0°, nearly 80 volumes SO_2. The coefficient of absorption, according to Bunsen and Schönfeld, at temperatures ranging between 0° and 20°, is

$$79{\cdot}789-2{\cdot}6077\,t+0{\cdot}029349\,t^2;$$

at temperatures between 21° and 40°,

$$75{\cdot}182-2{\cdot}1716t+0{\cdot}01903t^2.$$

The saturated acid contains at 0° 68·861 volumes of gaseous SO_2, and has a specific gravity of 1·06091; at 10° it contains 51·383 volumes gaseous SO_2, and has the spec. grav. 1·05472; at 20°, 36·206 volumes SO_2, spec. grav. 1·02386. The absorbed gas does not escape on freezing—and on boiling, only completely after a long time. Alcohol absorbs a much larger volume of sulphur dioxide (at 0° and 0·76 metre pressure, 338·62 volumes SO_2).

A table, not very much deviating from the above statements, of the solubility of sulphur dioxide in water at 0·76 metre mercurial pressure at different temperatures, is given in Kopp and Will's 'Jahresberichte' for 1861, p. 54.

Giles and Shearer (J. Soc. Chem. Ind. 1885, p. 305) give the following table of the precentage of SO_2 in solutions of various specific gravities:—

Temp.	Spec. grav.	Per cent. SO_2.	Temp.	Spec. grav.	Per cent. SO_2.
15°·5 C.	1·0051	0·99	15°·5 C.	1·0399	8·08
,,	1·0102	2·05	,,	1·0438	8·68
,,	1·0148	2·87	,,	1·0492	9·80
,,	1·0204	4·04	,,	1·0541	10·75
,,	1·0252	4·99	12°·5	1·0597	11·65
,,	1·0297	5·89	11°·0	1·0668	13·09
,,	1·0353	7·01			

Another table, for the temperature 15° C., is given by Scott (Pharm. Soc. J. & Trans. xi. p. 217) :—

Per cent. SO_2.	Specific gravity.	Per cent. SO_2.	Specific gravity.
0·5	1·0028	5·5	1·0302
1·0	1·0056	6·0	1·0328
1·5	1·0085	6·5	1·0353
2·0	1·0113	7·0	1·0377
2·5	1·0141	7·5	1·0401
3·0	1·0168	8·0	1·0426
3·5	1·0194	8·5	1·0450
4·0	1·0221	9·0	1·0474
4·5	1·0248	9·5	1·0497
5·0	1·0275	10·0	1·0520

Much higher are the figures given by Pellet (Journ. Soc. Chem. Ind. 1902, p. 171) :—

P. c. SO_2 in 100 H_2O	1	2	3	4	5	6
Sp. gr. at 15°–17° C.	1·0025	1·015	1·0225	1·030	1·0375	1·045.

An apparatus for the production of aqueous solutions of sulphurous acid has been described by Holzhäusel (G. P. no. 49194).

Solutions of sulphurous acid in the presence of oxygen are partly converted into sulphuric acid.

According to Scott, when sulphur dioxide (mixed with CO_2) is to be made by the process mostly used, viz. that of heating sulphuric acid with charcoal, it is best to employ acid of 74 per cent. SO_3=165° Tw. If stronger acid be used, a portion of it is reduced to sulphur, which may give iron sulphide with the iron of the apparatus; with weaker acid sulphuretted hydrogen is formed. In order to obtain the gas as pure as possible, the washing-water should be mixed with lead sulphate or coarsely powdered charcoal.

Sulphurous acid forms two series of salts (sulphites)—saturated or normal ones, SO_3M_2; and acid ones, SO_3MH, isomorphous with the corresponding carbonates.

Sulphur dioxide is absorbed by anhydrous barium oxide at 200°, better at 230°; by strontium oxide at 230°, better at 290°; in both cases the normal sulphite is formed. Calcium oxide forms at 400° a basic sulphite, $Ca_6S_5O_{16}$, which at 500° splits up into sulphate and sulphide. Magnesia absorbs SO_2 very slowly at 326°, and slightly above this the sulphate is formed (Birnbaum & Wittich, Ber. d. d. chem. Ges. 1880, p. 651).

The reactions taking place between sulphur dioxide and the oxides and acids of nitrogen will be described in a later part of this Chapter.

Injurious action of Sulphurous Acid (*Sulphur Dioxide*).—The quantity of SO_2 which may be present in the air without being injurious to health has been stated by Hirt ('Gewerbekrankheiten,' p. 15) = 1 to 3 per cent. This is an obvious error. Ogata (Archiv f. Hygiene, 1884, p. 223) found that 0·04 per cent. SO_2 causes difficulty of breathing after a few hours; he could not take a single full breath in air containing 0·05 per cent. SO_2. It is an acute blood-poison.

Lehmann (Zsch. f. angew. Ch. 1893, p. 612) shows that persons not habituated to sulphurous acid are very little affected by 0·012 per mille, but perceptibly so by 0·015 per mille SO_2. The presence of 0·030 per mille after a few minutes causes strong irritation of the nasal membranes, sneezing, and slight coughing, which symptoms decrease after 10 minutes. The employés and workmen accustomed to it are but little affected by 0·037 per mille; the sensibility to SO_2 seems to be lessened by habitually respiring air containing it.

Sulphur dioxide is also very injurious to vegetation, and is one of the chief constituents of the "noxious vapours" so much complained of in most manufacturing districts. It is true that these vapours contain other injurious constituents, chiefly of an acid character, viz. sulphuric anhydride, hydrogen chloride, and sometimes even the acids of nitrogen. Disregarding the latter, and even HCl, which will be treated of in the Chapter devoted to that subject, we shall now enter upon a description of the effects produced by the ordinary "acid smoke" of metallurgical and similar works, where SO_2, and generally also SO_3, are the principal acids concerned.

A detailed investigation of the influence of the noxious vapours at Freiberg, where very large and numerous smelting-works are situated, on vegetation and on the health of domestic animals has been made by Freytag (abstracted in Wagner's Jahresb. 1873, p. 180). The acid, arsenic, and zinc vapours of the Freiberg smelting-works under favourable circumstances, even with the present condensing arrangements, may injure the vegetation of the neighbourhood in the following way: at a sufficient concentration they are taken up by the leaves when covered with dew; on the evaporation of the water the organs affected are corroded and reduced to the same state as that which they assume when vegetation ceases. This injury can always be proved both by the eye and by chemical analysis. A "poisoning" of the soil or of the whole plant is out of the question. The assumption of an *invisible* injury done to the vegetation by the smelting-works' vapours and the awarding of damages founded thereon are unwarranted; they contradict the fundamental principles of all exact investigation and foster the desire of the unreasoning multitude to incessantly raise fresh claims for damage alleged to have been done by the works. A decrease of the nutritive value of food-plants, in cases of visible injury done to the leaves, can only occur in consequence of the loss of these leaves and the lessened ability of the plants to decompose carbonic acid and produce organic matter therefrom. Any metallic oxides or salts adhering to the leaves of food-plants may become dangerous to the animal organization by causing inflammation of the mucous membranes, and, under very unfavourable circumstances, may produce death; but this fact can always be established with certainty by *post-mortem* examination and by chemical analysis. The supposition that the "acid disease" and tuberculosis occurring in a particular neighbourhood among the cattle are produced by the noxious vapours from smelting-works is utterly unfounded and must be most emphatically contradicted. Freytag considers that air containing more than 0·003 volume per cent. of SO_2 will do injury to vegetation.

Schroeder (Wagner's Jahresber. 1874, p. 277) made extensive experiments on the influence especially of sulphurous acid on vegetation, with the following principal results:—From air containing as little as $\frac{1}{3000}$ of its volume of SO_2 this gas is absorbed by the leaves of "leafy" (deciduous) trees and conifers; these retain it mostly, a smaller portion penetrating into the wood, the bark, and the leaf-stalks, either as such or after oxidation to sulphuric acid. Conifer-leaves absorb less sulphurous acid from the air for an equal surface of leaves than deciduous trees; the absorption takes place equally over the whole surface of the leaf, not by the stomata, and therefore has no relation to the number of the latter. A principal effect of the injurious action of sulphurous acid is its causing a check to the normal evaporation of water, the disturbance being in a direct ratio to the quantity of SO_2; the evaporation is mostly affected by absorption of SO_2 in sunlight, at a high temperature and in dry air. The transpiration of conifers is not visibly lowered by the same quantity of sulphurous acid as that which affects other trees (deciduous ones). The injury done by sulphurous acid is greater if the absorption takes place at the lower than if at the upper side of the leaf.

Other communications on this subject, partly contradicting those of Schroeder, have been made by Stöckhart (Wagner's Jahresb. 1874, p. 228). According to his observations at Zwickau, a distance of 630 metres (=690 yards) protects even the most sensitive vegetation against the effect of large volumes of vapours, if they escape through chimneys not less than 82 feet high. Conifers are much more sensitive than deciduous trees; the decreasing series of sensibility is—pine, pitch-pine, Scotch fir, larch, hawthorn, white beech, birch, fruit-trees, hazel-nut, horse-chestnut, oak, red beech, ash, linden, maple, poplar, alder, mountain-ash. In the parts of plants corroded by sulphurous acid, not this acid, but sulphuric acid can be found, and that to a larger extent than in the same parts of plants collected at the same time in districts free from smoke.

Schroeder and Schertel (Wagner's Jahresb. 1879, p. 234) found in healthy fir-leaves 0·162 to 0·237 per cent. SO_3; damage was only done when the percentage rose above 0·250; the highest found was 0·592 near Freiberg, 1·33 in the Oberharz.

Other figures given by Fricke (Chem. Ind. 1887, p. 492) state the difference in the amount of SO_2 found in healthy and damaged plants as follows:—

	Healthy.	Damaged.
Beans …………	6·119	6·551
Buckwheat ……	5·110	5·880
Grass …………	7·105	8·336
Rye ……………	3·684	5·610
Wheat …………	2·179	4·412
Cabbage ………	27·290	30·843
Oats …………	2·926	6·788
Potatoes ………	13·000	17·500

In most cases the differences are too slight to base any trustworthy conclusions on them. Oats, wheat, and potatoes stand the acid gases better than young meadow-plants.

Just and Heine (Chem. Industrie, 1889, p. 252) also found very varying percentages of sulphuric acid in plants alleged to be damaged by SO_2, so that this means of tracing such injury is very unreliable.

F. Fischer, in the 230th volume of Dingler's Journal, has given a short synopsis of the researches made in this direction up to 1878. A special treatise (in German) has been published on acid smoke by Hering (Cotta, 1888).

Morren (Chem. Trade Journ. ii. p. 188) shows that leaves are more sensitive than flowers to sulphurous acid. When present in a proportion of 1-80,000 in the air, the leaves of fruit-trees are visibly affected in three to five hours, and this effect seems to spread after direct action of the gas ceases. Adult leaves are usually more sensitive than young leaves. The nerves are least affected and usually remain green. Sulphurous acid dissolved in water is almost without effect on the upper surface, whilst on the lower surface each little drop causes the formation of a spot visible on both surfaces. This solution is not quickly changed into sulphuric acid; the effect of the latter is quite different from that of sulphurous acid.

Koenig (Dingler's Journal, ccxxix. p. 299) describes the appearance of trees destroyed by the vapours from roasting blende.

Hasenclever (Chem. Ind. 1879, p. 22·) gives coloured and photolithographic illustrations of the ravages caused by acid vapours and metallic sulphates upon the leaves of plants and plantations of trees, side by side with those caused by frost, autumnal decay, fungi, drought, overgrowth of other trees, &c.,

which closely resemble the phenomena produced by the acid vapours from chemical works, and hence are frequently wrongly attributed to the latter cause. Neither is the estimation of sulphates and chlorides in the damaged leaves &c. at all a safe guide to the detection of the real cause, looking at the enormous quantity of acids sent into the air wherever coal is consumed on a large scale. At Stolberg, near Aachen, on a superficial area of 1600 acres, 220 chimneys daily emit 34½ tons of sulphur dioxide from coal, and nearly 51 tons of SO_2 from zinc-works, glass-works, &c., the alkali-works adding only ½ ton (more correctly 480 kilog.) of SO_2, and ¾ ton of HCl. Hence alkali-makers ought not to be saddled with the whole, or even the chief part, of the damage observed in the neighbourhood.

An important paper on the subject in question has been published by Hamburger (Journ. Soc. Chem. Ind. 1884, p. 202). His conclusions, founded upon a large number of analyses of damaged leaves, are practically the same as Hasenclever's, namely, that undoubtedly injury is done to vegetation by the acids in the smoke; but much difficulty exists as to proving this with certainty in special cases, and at all events the SO_2 contained in ordinary coal-smoke contributes very largely to the injurious action popularly attributed to the emanations from chemical works.

A professional forester, Reuss, partly by himself and partly together with Schroeder, has embodied the results of laborious work on this subject in several German publications. Their conclusions have been attacked by another forester, Borggreve, but Hasenclever (Chem. Ind. 1895, p. 496) has shown many mistakes in that criticism. They all agree in the conclusion that the growth of trees is only impeded by acid vapours if *visible* damage is done to the leaves. When the leaves or needles remain green, chemical analysis may prove an action of acid gases, but no real damage.

Winkler (Zsch. angew. Ch. 1896, p. 371) ascribes the effect of noxious vapours from brick-kilns &c. principally to their containing aqueous vapour, which, on cooling, causes the condensation of sulphurous and hydrochloric acid.

Further papers on noxious vapours, with details as to their action, are those by Hagen (Chem. Zeit. 1896, p. 238), Ost (ibid. 1896, p. 165), Nissenson and Neumann (Berg- u. Hüttenm. Zeit. 1896, p. 145), Schröder & Schmitz-Dumont (Dingler's Journ. ccc.

p. 65), Ost and Wehmer (Chem. Ind. 1899, p. 233), Seydler (Fischer's Jahresb. 1899, p. 358), Ramann and Sorauer (ibid. 1900, p. 332), Wislicenus (Zsch. ang. Ch. 1901, p. 689).

Detection and Estimation of Sulphurous Acid and Sulphur Dioxide.

Qualitative reactions of Sulphurous Acid.—The sense of smell is a very good means for detecting the presence of SO_2, when other odorous acids are absent. Gaseous mixtures containing SO_2 together with such acids are best passed through an absorbent, *e.g.* sodium carbonate, with which afterwards the ordinary reactions for SO_2 are made. When passing such gaseous mixtures through a solution of potassium permanganate, or of iodine in potassium iodide, these liquids are decolorized, the iodine being reduced to HI. This last reaction may also be utilized on test-paper. On the other hand, a test-paper, soaked in a solution prepared by boiling 2 grams wheat-starch with 100 c.c. of water, and adding 0·2 gram of potassium iodate dissolved in 5 c.c. water, is turned blue by SO_2, by the formation of free iodine. These reactions may also be utilized for recognizing the presence of SO_2 when set free from its salts by the action of sulphuric acid. One of the best reactions, and one specially adapted for discovering SO_2 in sulphuric acid itself, is its conversion into H_2S by means of pure zinc, or, preferably, aluminium in an acid solution. The H_2S is then recognized by its reaction on lead paper, or by the purple colour produced in an ammoniacal solution of sodium nitroprusside.

A solution of a sulphite, either neutral or with addition of some sodium bicarbonate (*just* acidulated with acetic acid), when poured into a solution of zinc sulphate containing a little sodium nitroprusside, produces a red colour or precipitate, either at once or, if very little SO_2 is present, after adding some potassium ferricyanide. This reaction is not given by thiosulphates, which are, moreover, distinguished from sulphites by their giving (generally only after a little time) a precipitate of sulphur on being treated with a stronger acid. According to Reinsch, SO_2 can be detected by boiling the acid solution with a strip of clean copper, which is thereby blackened. This is caused by the formation of cupric sulphide, and the colour is not changed by heating the strip in a glass tube; but when the colour is produced by arsenic, there is a sublimate of white arsenious acid formed in the tube.

According to Schützenberger, sulphurous acid contained in a solution can be recognized by adding a very little indigo solution and agitating with a zinc rod; owing to the formation of hyposulphurous acid (Schützenberger's "hydrosulphuric" acid), HSO_2, the blue colour will be destroyed, but will quickly reappear in contact with the air.

The *quantitative estimation* of sulphurous acid in the free state can take place either as will be described in the case of sulphites, or by titration with standard alkali. In the latter case, however, it must be noted that the point of neutrality is reached with phenolphthalein when the normal salt, Na_2SO_3, has been formed, so that each c.c. of normal alkali (containing 0·031 NaOH) indicates 0·032 SO_2. Of course, as is always the case with phenolphthalein, the standard alkali must be soda or potash, ammonia being useless for this purpose. But when employing methyl-orange as indicator, the point of neutrality is reached exactly at the formation of $NaHSO_3$, so that each c.c. of normal alkali indicates 0·064 SO_2. Litmus gives somewhat uncertain results, and is therefore useless as an indicator. It is thus possible to estimate free SO_2 in the presence of stronger free acids in this way: one portion of the liquid is titrated with methyl-orange, and another with phenolphthalein as indicator; in the latter case more alkali will be used, and the difference of c.c. of normal alkali, multiplied by 0·064, shows the quantity of free SO_2 present (Lunge, J. Soc. Chem. Ind. 1883, p. 513; Thomson, Chem. News, xlvii. p. 136; Blarez, in Compt. Rend. ciii. p. 69, adduces nothing new).

The acid sulphites are neutral to methyl-orange, which consequently allows us to estimate any SO_2 present over and above $NaHSO_3$. The SO_2 present in the $NaHSO_3$ itself can be titrated with normal soda and phenolphthalein, each c.c. of normal alkali indicating 0·064 SO_2. Normal sulphites, as Na_2SO_3, can be titrated by means of methyl-orange and standard hydrochloric or sulphuric acid, the red colour appearing when $NaHSO_3$ has been formed, so that each c.c. of standard acid indicates 0·064 SO_2.

Other methods of estimating SO_2 either in the free state or in its salts are based on its reducing properties. The reagents serving for this purpose are either a standard solution of iodine or one of potassium permanganate, both of which are well known and require no description here. A decinormal solution of either indicates per cubic centimetre 0·0032 gram SO_2. The method to be recommended for testing gaseous SO_2 in burner-gas will be described when treating of that gas. Special attention must be drawn to the necessity of employing water *free from air* in estimating SO_2. This is not necessary if the solution of the sulphite or sulphurous acid is run into the solution of iodine (Giles and Shearer, J. Soc. Chem. Ind. 1884, p. 197, and 1885, p. 303).

In many cases the quantitative estimation of sulphurous acid can take place by converting it into sulphuric acid by means of oxidizing agents: chlorine, bromine, iodine, hydrogen peroxide, &c. The sulphuric acid is then estimated in the usual way.

Sulphur dioxide in the presence of hydrogen sulphide, which gases may exist together in a state of great dilution by inert gases (as in the exit-gases from "Claus kilns"), can be estimated by passing the gases through a solution of I in KI, followed by one of caustic soda or, preferably, sodium thiosulphate. The iodine oxidizes H_2S into H_2O+S, and SO_2 into H_2SO_4; hence the acidity of the solution is not affected by H_2S, merely by SO_2. On the other hand, each c.c. of decinormal iodine indicates 0·0032 gram of sulphur in either case, so that the difference between the iodometrical and the alkalimetrical test gives the H_2S present. The addition of a tube with sodium thiosulphate solution is necessary, because the gaseous current carries away some iodine which is retained in that solution; the latter, before titrating the iodine solution back, is added to it (details in my paper, J. Soc. Chem. Ind., Nov. 1890).

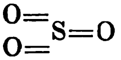
Applications of Sulphurous Acid (*Sulphur dioxide*).

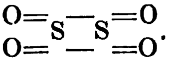
The greatest quantity of SO_2 is produced for the manufacture of sulphuric acid. Next to this in importance comes its use for the manufacture of wood-pulp, mostly in the state of calcium bisulphite (or a solution of $CaSO_3$ in an excess of sulphurous acid). One of the oldest uses of sulphur dioxide, in the shape of burning sulphur, is as a disinfecting and antiseptic agent. For the former purpose it is not so much valued now as formerly, since it has been shown that many of the disease-germs resist the action of SO_2 for a long time. The antiseptic function of SO_2 comes into play in the fumigation of wine-casks, in the arresting of the fermentation of wort, in the manufacture of glue (where it acts also as a bleaching agent), and in many other cases.

In the textile industries sulphurous acid is largely used as a bleaching agent, especially for wool, silk, straw, &c. It is not quite certain in which way it acts in this case, possibly by forming a compound with the colouring-matters contained in the fibres. Formerly it was generally assumed that the SO_2 in bleaching acted as a reducing agent, which indeed must be true in some cases, although probably not in all. The reducing functions of SO_2 are utilized in chemical and metallurgical operations in too many cases to be enumerated here.

SULPHURIC ANHYDRIDE, SO_3
(Sulphur Trioxide),

consists of 40 per cent. by weight of sulphur, and 60 per cent. of oxygen. According to Marignac (Arch. Sci. Phys. Nat. xxii. p. 225, 1853; lii. p. 236, 1875; lviii. p. 228, 1877) and Schultz-Sellack (Berl. Ber. iii. p. 215), it exists in two different modifications, a liquid and a solid. The liquid, α-anhydride, melts at +16° C., and begins to boil at +35° (according to Schultz-Sellack, at 46°). Spec. grav. at 13° = 1·9546, at +20° (melted) = 1·97. In the melted state it is less oily than oil of vitriol, and, if pure, colourless, but usually coloured brown by dust. When kept for some time at the ordinary temperature (below 25°) it is changed into the solid, β-anhydride, whose melting-point is stated very differently, from 50° to 100° C. Probably it begins to melt at 50°, and gradually passes over into the α-modification; it slowly evaporates, even at the ordinary temperature. It forms fine, feathery, asbestos-like, white needles. The β-anhydride is probably a polymer of the α-modification. Buff (Ann. Chem. Pharm., Suppl. iv. p. 151) confirms this. According to R. Weber, however (Poggendorff's Ann. clix. p. 313; Berl. Ber. xix. p. 3187), the sulphur trioxide, obtained absolutely pure and free from water by his method, is at the summer temperature a very mobile, colourless liquid, which, on gradually cooling, solidifies to long, transparent, prismatic crystals similar to nitrate of potash, quite different from the white, opaque crystals of the ordinary anhydride containing a little water. These crystals melt at 14°·8 C., and boil at 46°·2. Under certain conditions the anhydride can, like many other bodies, be cooled much below its proper melting-point without solidifying, but then solidifies suddenly. After a twelvemonth it still shows the same composition and the same melting-point as it had when freshly prepared. Weber accordingly rejected the assumption of two different modifications, and ascribes the phenomena of this kind observed by others, especially the formation of the modification resembling asbestos, to a minute residue of water. So much seems to be correct in Weber's conclusions that the transition of the first to the second modification is promoted by a minute quantity of water.

Oddo, in 1901 (Rend. Acc. Lincei, [5] x. p. 207; Chem. Centralbl. 1901, i. p. 969), definitely proved the existence of two modifications by cryoscopic estimation of the molecular weights. The compound melting at 13°·8 is the real sulphur trioxide, SO_3; the fibrous compound, which does not melt unchanged, but at 50° slowly, and at 100° quickly changes into SO_3, is disulphuric anhydride, S_2O_6. SO_3 instantly burns organic tissues and causes deep wounds; S_2O_6 is much less active and can be touched with the hand. SO_3 dissolves at once in H_2SO_4; S_2O_6 but slowly. Oddo gives the structural formula of SO_3:  $\begin{matrix}O=\\O=\end{matrix}S=O$;

of S_2O_6:  $\begin{matrix}O=\\O=\end{matrix}S\begin{matrix}-\\-\end{matrix}S\begin{matrix}=O\\=O\end{matrix}$.

Schenck (Lieb. Ann. cccxvi. p. 1) regards the liquid modification as a solution of the asbestos-like polymer in real SO_3 in a state of unstable equilibrium.

The heat of formation of one molecule of SO_3 (=80 parts by weight) from S and O_3 is = 103,230 cals. (Thomsen); from $SO_2 + O$ = 34,400 cals. in the solid state, or = 22,600 cals. in the gaseous state (Berthelot). The heat of vaporizing 1 mol. SO_3 is = 11,800 cals.; that produced by dissolving 1 mol. SO_3 in a large quantity of water = 39,170 cals. (Thomsen).

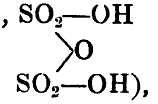
In moist air sulphuric anhydride at once forms dense white fumes; with water it hisses like red-hot iron. Many organic substances are at once charred by it. In the complete absence of water it does not redden litmus. It gives several compounds with sulphur, whose colour, with the quantity of sulphur decreasing, changes from brown to green and blue. In the blue modification Weber has proved the presence of the sesquioxide, S_2O_3. With sulphur dioxide there seems to exist a distinct compound, $SO_2 + 2\,SO_3$. With water SO_3 at once combines to form sulphuric acid (SO_4H_2) and its different hydrates. It is, however, not easy to completely condense the sulphuric anhydride often produced in considerable quantity in technical processes, even with a large quantity of water and manifold contact, and special precautions have to be taken for this purpose.

The anhydride SO_3, when conducted through a red-hot tube, splits up into SO_2 and O, but is reformed from these gases at a somewhat lower temperature, especially in the presence of platinum and several metallic oxides. The technical application of this reaction is described in Chapter XI.

For scientific purposes sulphuric anhydride is made by gently heating fuming oil of vitriol, or by igniting sodium pyrosulphate ($Na_2S_2O_7$). Its production in a perfectly pure state is described by Weber (*l. c.*). Formerly it was not used for technical purposes, owing partly to the costliness of its production, partly to the supposed difficulty of handling and keeping it. Recently, however, its production has been made so much cheaper that certain branches of manufacture already employ it advantageously. Its application has turned out to be a very simple affair, as it can be sent out in drums made of tinned iron. Its handling is certainly unpleasant, since the contact of the skin with liquid anhydride, or even just liquefying by absorbing moisture, causes very malignant and slow-curing burns. Its production on a manufacturing scale will be described in Chapter XI.

PYROSULPHURIC ACID, $S_2O_7H_2$

(Structural formula,



$$\begin{array}{l} SO_2\text{—}OH \\ \quad \rangle O \\ SO_2\text{—}OH \end{array}$$

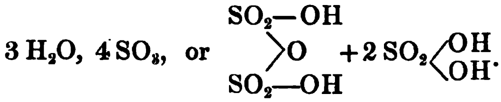
),

contains the elements of 89·89 parts of sulphuric anhydride and 10·11 of water, or equal molecules of hydrate and anhydride. A transparent crystalline mass, melting at 35° C., it decomposes at moderate heat into anhydride (SO_3) and oil of vitriol (SO_4H_2).

Pyrosulphuric acid is contained in the Nordhausen fuming acid of trade, which often consists altogether of it, and then bears the trade name "solid oleum." Pyrosulphuric acid can also be easily obtained from the ordinary liquid fuming Nordhausen acid by cooling below 0°. Lastly, it can be made by carefully mixing anhydride with a small quantity of oil of vitriol. Weber (*l. c.*) obtained an intermediate hydrate, H_2SO_4, 3 SO_3, corresponding to 94·69 per cent. of SO_3.

Pyrosulphuric acid forms salts, of which those of the alkaline metals are the best known and most important. This sodium pyrosulphate ($S_2O_7Na_2$) is formed by fusing acid sodium sulphate (SO_4NaH) at incipient red-heat. At a full red-heat it splits up further into neutral sulphate (SO_4Na_2) and sulphuric anhydride (SO_3); this reaction is sometimes utilized for producing the latter compound. In contact with water, the pyrosulphates are gradually retransformed into acid sulphates.

A compound with 14·44 per cent. H_2O can also be obtained, which crystallizes in thin transparent prisms, fumes in the air, and melts at 26° C. Formula—



$$3\,H_2O,\ 4\,SO_3,\ \text{or}\ \begin{matrix} SO_2\text{—}OH \\ \rangle O \\ SO_2\text{—}OH \end{matrix} + 2\,SO_2\begin{matrix} \diagup OH \\ \diagdown OH \end{matrix}.$$

The Nordhausen or *fuming oil of vitriol,* the manufacture of which will be described in the 11th Chapter, is a viscous oil, representing a mixture of pyrosulphuric acid or sulphur trioxide with sulphuric hydrate in varying proportions, and therefore solidifying at very different temperatures. It fumes in the air, and gives out vapours of anhydride, whilst monohydrate remains behind. Water transforms it at once into ordinary sulphuric acid, with strong evolution of heat. It is often coloured brown by organic substances, and, according to its mode of preparation, contains many other impurities, such as iron, sodium, calcium, aluminium, &c. (as sulphates), sulphurous acid, selenium, organic matters, &c. When the receivers used in its preparation are charged with ordinary strong acid, the impurities of the latter will likewise pass into the fuming acid.

The subjoined tables refer to the mixtures of SO_3 and H_2SO_3, comprised under the designation of *fuming oil of vitriol* (abridged O.V.), even when they consist mostly of SO_3 and are solid at the ordinary temperatures.

Melting-points of fuming O.V.

Knietsch (Ber. 1901, p. 4100) gives the following table of the fusing-points of fuming sulphuric acid (comp. also under "Sulphuric Acid" below) :—

Per cent. SO_3.	Melting-point ° C.	Per cent. SO_3.	Melting-point ° C.
0	+10·0	55	+18·4
5	+ 3·5	60	+ 0·7
10	− 4·8	65	+ 0·8
15	−11·2	70	+ 9·0
20	−11·0	75	+17·2
25	− 0·6	80	+22·0
30	+15·2	85	+33·0 (27·0)*
35	+26·0	90	+34·0 (27·7)
40	+33·8	95	+36·0 (26·0)
45	+34·8	100	+40·0 (17·7)
50	+28·5		

The *boiling-points* of fuming O.V. are stated by Knietsch (*l. c.* p. 4110) as follows :—

SO_3 total per cent.	SO_3 free per cent.	Boiling-point ° C.	Barometric pressure, mm.
82·3	3·64	212	759
83·4	9·63	170	759
86·45	26·23	125	759
89·5	42·84	92	759
93·24	63·20	60	759
99·5	97·2	43	759

The *vapour-pressures* of various descriptions of fuming O.V. are given in the same place; comp. also the curves, *infrà*, p. 174.

Specific gravities of fuming O.V.

Cl. Winkler gives the following table of the specific gravities of fuming sulphuric acid at 20° C.; but it should be remarked that he worked only with "commercial acid," made by the old process, and that consequently all the densities found are sensibly higher than those belonging to pure acids; nor is it a matter of surprise that the values found by Messel with another description of

---

* The numbers in brackets denote the fusing-points of fresh, not yet polymerized acids.

"commercial acid" (see below) do not entirely agree with Winkler's table.

Specific gravity at 20° C.	Percentage of		Percentage of		Percentage of	
	SO_3.	H_2O.	SO_3.	acid of 66° B.	free SO_3.	H_2SO_4.
1·860	81·84	18·16	26·45	73·55	1·54	98·46
1·865	82·12	17·88	27·57	72·43	2·66	97·34
1·870	82·41	17·59	28·76	71·24	4·28	95·76
1·875	82·63	17·37	29·95	70·05	5·44	94·56
1·880	82·81	17·19	30·38	69·62	6·42	93·58
1·885	82·97	17·03	31·03	68·97	7·29	92·71
1·890	83·13	16·87	31·67	68·23	8·16	91·84
1·895	83·43	16·66	32·52	67·48	9·34	90·66
1·900	83·48	16·52	33·09	66·91	10·07	89·93
1·905	83·57	16·43	33·46	66·54	10·56	89·44
1·910	83·73	16·27	34·10	65·91	11·43	88·57
1·915	84·08	15·92	35·52	64·48	13·33	86·67
1·920	84·56	15·44	37·27	62·73	15·95	84·05
1·925	85·06	14·94	39·49	60·51	18·67	81·33
1·930	85·57	14·43	41·56	58·44	21·34	78·66
1·935	86·23	13·77	44·23	55·77	25·65	74·35
1·940	86·78	13·22	46·46	53·54	28·03	71·97
1·945	87·13	12·87	47·88	52·12	29·94	70·06
1·950	87·41	12·59	49·01	50·99	31·46	68·54
1·955	87·65	12·35	49·98	50·02	32·77	67·23
1·960	88·22	11·78	52·29	47·71	35·87	64·13
1·965	88·93	11·08	55·13	44·87	39·68	60·32
1·970	89·83	10·17	58·81	41·19	44·64	55·36

Messel (J. Soc. Chem. Ind. 1885, p. 573) gives the following specific gravities of commercial Nordhausen acids, both at 26°·6 C., as determined by himself, and calculated for 15°·5 C.:—

Specimens.	Percentage of SO_3.	Specific gravities	
		at 80° F. (=26°·6C.)	calculated for 60° F. (=15°·5C.)
Liquid	8·3	1·842	1·852
"	30·0	1·930	1·940
Crystalline mass, resembling nitre...	40·0	1·956	1·970
" " " ...	44·5	1·961	1·975
" " " ...	46·2	1·963	1·977
" " " ...	59·4	1·980	1·994
Liquid	60·8	1·992	2·006
"	65·0	1·992	2·006
"	69·4	2·002	2·016
Crystallized	72·8	1·984	1·988
"	80·0	1·959	1·973
"	82·0	1·953	1·967

Knietsch (Ber. 1901, p. 4101) gives the following tables for commercial fuming O.V., made by the contact process. The weighings were made at 15°, referred to water of 15°, with brass weights without reduction to a vacuum.[*] The temperatures to which they refer are 35° and 45° for fuming O.V., and 15° for this and the strongest ordinary acids.

The curves (p. 174) show a maximum for ordinary acid slightly *below* the percentage of monohydrate (H_2SO_4); for fuming acids the maximum is at 60 per cent. free SO_3 at 15° C., at 56 per cent. SO_3 at 35° C., at 50 per cent. SO_3 at 45° C.

Specific gravities at 15° and 45° C.

H_2SO_4 per cent.	Total SO_3 per cent.	Free SO_3 per cent.	Spec. grav. at 15° C.	Spec. grav. at 45° C.
95·98	78·35	......	1·8418	......
96·68	78·92	......	1·8429	......
96·99	79·18	......	1·8431	......
97·66	79·72	......	1·8434 Max.	......
98·65	80·53	......	1·8403	......
99·40	81·14	......	1·8388 Min.	......
99·76	81·44	......	1·8418	......
100·00	81·63	0·0	1·8500	1·822
......	83·46	10·0	1·888	1·858
......	85·30	20·0	1·920	1·887
......	87·14	30·0	1·957	1·920
......	88·97	40·0	1·979	1·945
......	90·81	50·0	2·009	1·964 Max.
......	92·65	60·0	2·020 Max.	1·959
......	94·48	70·0	2·018	1·942
......	96·32	80·0	2·008	1·890
......	98·16	90·0	1·990	1·864
.....	100·00	100·0	1·984	1·814

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[*] The values for acids of 100 per cent. H_2SO_4 and below do not quite agree with those found by Lunge and Naef (comp. later on), which could not be otherwise, as the latter worked with *pure* acids and referred their figures to water of 4° C. and to the vacuum. The only essential deviation is that Knietsch does not, like the authors mentioned, as well as Kohlrausch and Schertel, find the minimum spec. gravity at 100 per cent. H_2SO_4, but at 99·40 per cent.

Specific gravities of fuming O.V. at 35° C.

Total SO_2 per cent.	Free SO_3 per cent.	Spec. grav.	Total SO_3 per cent.	Free SO_3 per cent.	Spec. grav.
81·63	0	1·8186	91·18	52	1·9749
81·99	2	1·8270	91·55	54	1·9760
82·36	4	1·8360	91·91	56	1·9772
82·73	6	1·8425	92·28	58	1·9754
83·09	8	1·8498	92·65	60	1·9738
83·46	10	1·8565	93·02	62	1·9709
83·82	12	1·8627	93·38	64	1·9672
84·20	14	1·8692	93·75	66	1·9636
84·56	16	1·8756	94·11	68	1·9600
84·92	18	1·8830	94·48	70	1·9564
85·30	20	1·8919	94·85	72	1·9502
85·66	22	1·9020	95·21	74	1·9442
86·03	24	1·9092	95·58	76	1·9379
86·40	26	1·9158	95·95	78	1·9315
86·76	28	1·9220	96·32	80	1·9251
87·14	30	1·9280	96·69	82	1·9183
87·50	32	1·9338	97·05	84	1·9115
87·87	34	1·9405	97·45	86	1·9046
88·24	36	1·9474	97·78	88	1·8980
88·60	38	1·9534	98·16	90	1·8888
88·97	40	1·9584	98·53	92	1·8800
89·33	42	1·9612	98·90	94	1·8712
89·70	44	1·9643	99·26	96	1·8605
90·07	46	1·9672	99·63	98	1·8488
90·44	48	1·9702	100·00	100	1·8370
90·81	50	1·9733			

The *specific heats* were found by Knietsch as follows (those marked * were directly observed) :—

Total SO_3 per cent.	Free SO_3 per cent.	Spec. heat.	Total SO_3 per cent.	Free SO_3 per cent.	Spec. heat.
76·8	......	0·3691 *	91	51·0	0·370
78·4	......	0·3574 *	92	56·45	0·400
80	......	0·350	93	61·89	0·425
80·0	......	0·3574 *	93·3	63·5	0·4325 *
81·5	......	0·3478 *	94	67·34	0·455
82	2·0	0·345	94·64	70·6	0·4730 *
83·46	10·0	0·3417 *	95	72·78	0·495
84	12·89	0·340	96	78·23	0·535
85·48	20·95	0·3391 *	96·52	81·0	0·5598 *
86	23·78	0·340	97	83·67	0·590
87·13	29·74	0·3392 *	97·92	88·6	0·6526 *
88	34·67	0·350	99	89·12	0·650
88·75	38·75	0·3498 *	99	94·56	0·710
90	45·56	0·360	99·8	98·9	0·7413 *
90·1	46·1	0·3599 *	100	100·0	0·770
90·73	49·4	0·3660 *			

The *heats of solution* were observed by Knietsch both by means of a calorimeter and on a large scale. Those referring to fuming O.V. are given here, those of ordinary sulphuric acid under that heading.

SO_3 total per cent.	SO_3 free per cent.	Calories.	Heat of solution of *solid* O.V.
82	2·0	199	......
83	7·5	210	......
84	12·9	223·5	......
85	18·3	237·5	......
86	23·5	250	......
87	29·2	265	......
88	34·7	278	......
89	40·1	292	......
90	45·6	308	286
91	51·0	325	304
92	56·4	344	322
93	61·9	363	340
94	67·3	381	360
95	72·8	401	380
96	78·3	421	402
97	83·7	442	423
98	89·1	465	442
99	94·6	490	463
100	100·0	515	486

Knietsch (*loc. cit.*) gives also tables of the *electrical resistance*, the *velocity of outflow* (viscosity), and the *capillary rising* of sulphuric acids and O.V. from 0 per cent. to 100 per cent. SO_3; the results are exhibited in the curves, *infrà*, p. 174.

The action of fuming O.V. on *iron* (cast iron, wrought iron, and steel) will be mentioned later on, together with that of ordinary acids.

The *analysis* of fuming sulphuric acid is described after that of ordinary acid.

SULPHURIC ACID, H_2SO_4.

Natural Occurrence.

Free sulphuric acid is found very exceptionally in nature, whilst some sulphates, especially that of calcium, occur in enormous quantities.

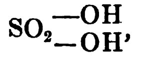
In the free state sulphuric acid has been found especially in a few springs of volcanic origin, and in the rivers fed by those springs. One of the best known cases of this kind is the Rio Vinagre in Mexico, which contains 0·111 per cent. free sulphuric acid (calculated as SO_3), and 0·091 per cent. free HCl; it daily carries into the sea 38 tons, according to others even 69 tons of both acids. Many other similar instances have been discovered in various parts of the world (comp. the first edition of this work, i. p. 17). Other cases again occur from the oxidation of sulphur ores, the acid being expelled by heat from the sulphates generated atfirst.

Miners are only too familiar with the occurrence of free acid in pit-waters from similar causes, by the corrosion of metal pumps and steam-boilers; even the leather of the valves thereby becomes brittle and the wooden parts are charred. In the case of volcanoes, sulphuric acid is formed by the oxidation of the sulphuretted hydrogen and the sulphur dioxide from the fumaroles and solfataras.

Even in the animal kingdom free sulphuric acid has been found, viz. in the salivary glands of several mollusks, especially of *Dolium galea*, which contain 2·47 per cent. free sulphuric acid and 0·4 per cent. free hydrochloric acid (Boedeker and Troschel; De Luca and Panceri).

Monohydrated Sulphuric Acid, H_2SO_4.

The proper sulphuric hydrate, commonly known as monohydrated sulphuric acid, has the rational formula :—



$$SO_2{\begin{matrix}-OH\\-OH\end{matrix}},$$

and may be considered as containing 81·63 per cent. SO_3 and 18·37 per cent. water. It is a limpid, colourless, oily liquid. Its specific gravity at 0^{c} is 1·853; at 15° (compared with water of 4°): 1·8384 (Lunge and Naef), 1·8378 (Schertel), 1·8372 (Marignac, F. Kohlrausch, Mendelejeff) *. The specific gravity changes to the extent of $\pm 0·001$ for each degree Centigrade. Both the addition of very little SO_3 and that of very little water raises the specific gravity (see below). The pure monohydrate solidifies at about 0° and forms large, plate-shaped crystals which melt at $+10^{\circ}·5$; they remain liquid a good deal below that temperature, but solidify on agitation, or even better when a fragment of the solid hydrate is introduced. The acid begins to boil at 290°, but the boiling-point rises up to 338° (Marignac). This shows that it does not distil unchanged: in fact a mixture of hydrated acid,

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* Comp. Berl. Ber. 1884, pp. 1748, 2536, 2711.

anhydride, and water passes over (see below). This dissociation begins much earlier; the pure monohydrate fumes, that is gives off SO_3, very slightly even at the ordinary summer temperature, distinctly at 30° or 40°. Accordingly it cannot be obtained by boiling down or distilling dilute acid, but by adding an exactly sufficient quantity of anhydride to the strongest acid obtainable by concentration, or by cooling such acid below 0° and several times recrystallizing the monohydrate in the same way. The latter process has been made commercially available by the Author for the manufacture of monohydratic sulphuric acid, which consequently is no longer a laboratory product, but has become an important article of commerce (comp. Chap. IX.).

The *vapour* of sulphuric acid consists for the most part, or even entirely (according to the temperature), not of molecules of SO_4H_2, but of isolated molecules of SO_3 and H_2O; theory would give to SO_4H_2 (2 vols.) a vapour-density of 3·862, for separated molecules of SO_3 and H_2O (4 vols.) a vapour-density of 1·6931, whilst Deville and Troost at 440° found it actually $=1·74$. The dissociation is therefore as good as complete in the state of vapour; and this assumption agrees very well with our present notions concerning the state of vapour (Dittmar, Chem. News, xx. p. 258).

Formation of Sulphuric Acid.—It has been asserted that sulphuric acid is formed in damp flowers of sulphur, even at the ordinary temperature; this is certainly the case on heating sulphur with water at 200° C., or by applying the electric current. Sulphur is easily oxidized to sulphuric acid by chlorine, hypochlorous acid, nitric acid, aqua regia, &c. It is produced, along with sulphurous acid and sulphur, from tri-, tetra-, and pentathionic acids—from the former by merely heating, from all three by the action of chlorine or bromine, or even on the prolonged action of stronger acids, which set the thionic acids free; also the thiosulphates yield sulphuric acid under the action of chlorine. All these decompositions have to be kept in view in alkali-making.

Mostly sulphuric acid is formed from sulphur dioxide. The aqueous solution of the latter is gradually transformed into sulphuric acid by the action of the air alone, and it is so transformed at once by chlorine, bromine, iodine, hypochlorous acid, nitric acid, and several metallic salts, such as manganic sulphate, mercurous nitrate, &c. Sulphur dioxide and oxygen conducted through a red-hot tube containing platinum, platinized asbestos, ferric oxide, and a number of other substances, yield sulphuric anhydride, or in the presence of water sulphuric acid. This reaction, which was formerly only of scientific interest, has become of the greatest technical importance and is, according to some opinions, destined to supersede the formerly universal, and, up to this, most general process of making sulphuric acid from sulphur dioxide, air, and water by means of nitrogen oxides as oxygen carriers. All this will be explained in detail later on.

The heat of formation of 98 parts SO_4H_2 is :—

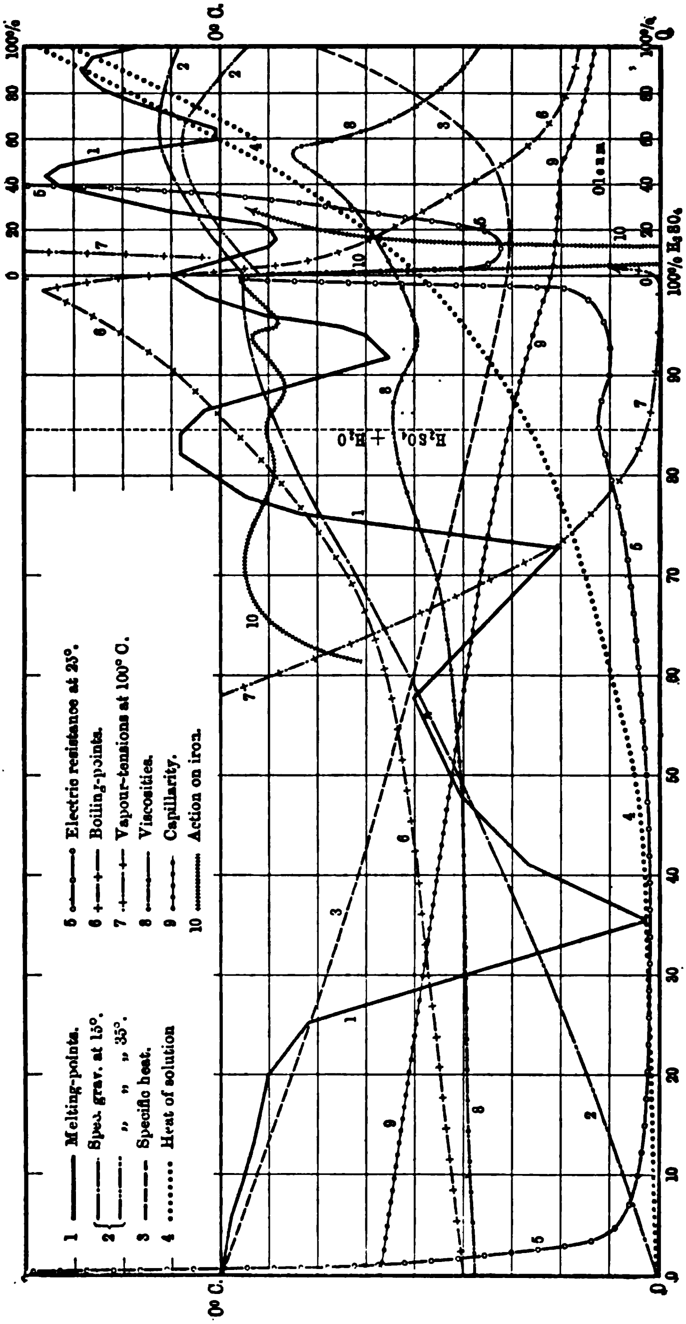
	Liquid.	In diluted solutions.
From SO_2, O, H_2O......	54,400	72,000 calories.
„ S, O_3, H_2O	124,000	141,000 „
„ S, O_4, H_2	193,000	210,000 „

The heat of neutralization of 1 mol. (98 parts) H_2SO_4 by 2 mols. (80 parts) NaOH in the presence of 400 mols. of water is given by Thomsen =31,380 cals. Pickering (Journ. Chem. Soc. 1889, p. 323) states it only =28,197 cals.

Sulphuric acid containing water.—The strongest oil of vitriol obtainable by boiling-down ordinary pure sulphuric acid contains a quantity of water which is not stated alike by different observers (Marignac, Pfaundler, Roscoe, Dittmar, Lunge and Naef, &c.). The statements differ from 97·86 to 98·99 per cent. of SO_4H_2; it is at all events very nearly 98·3 per cent. This *distilled sulphuric acid* solidifies a little below 0°; but it also shows the phenomenon of superfusion in a very high degree. It boils at 338° (Marignac), or 315° to 317° C. (Pfaundler and Pölt). Usually Marignac's statement is considered the most reliable; the acid of Pfaundler and Pölt probably contained a little more water. The boiling takes place quietly under a stronger pressure than the ordinary one, but at a lower pressure with violent bumping, which can be avoided by putting in platinum wire or scraps, according to Dittmar even better by conducting a slow current of air through it during the boiling (see Chapter VIII., purification of sulphuric acid).

This acid of 98·3 per cent. H_2SO_4, distilling unchanged, possesses a number of other peculiarities, marking it out as representing a certain equilibrium, or so-called "critical concentration." This comes out very well in a series of curves, given by Knietsch (Ber. 1901, p. 4089), fig. 39, p. 174. The boiling-points at that point

Fig. 39.


1 Melting-points.
2 Spec. grav. at 15°.
,, ,, ,, 35°.
3 Specific heat.
4 Heat of solution
5 Electric resistance at 25°.
6 Boiling-points.
7 Vapour-tensions at 100° C.
8 Viscosities.
9 Capillarity.
10 Action on iron.
0 10 20 30 40 50 60 70 80 90 100% H_2SO_4
0 20 40 60 80 100% Oleum
0° C.
$H_2SO_4 + H_2O$

(330°) show a sharp apex; below this, water or dilute sulphuric acid, above this, sulphuric anhydride is volatilized until in either case the constantly boiling acid of 98·3 per cent. is reached. The vapour-tension at that critical concentration is = zero, measured at 100° in a vacuum; the specific gravity of hydrated acid here reaches its maximum, from which it descends in both directions; the electrical resistance at this point begins to increase suddenly towards a maximum reached at nearly 100 per cent. H_2SO_4; in connection with this the action upon iron decreases, which is of great importance for the durability of apparatus (comp. below).

In fig. 39, curve 1, marked ——, shows the melting-points; curve 2, —·—·—· the specific gravities at 15°, —··—·· at 35°; curve 3, — — —, the specific heats; curve 4, ·····, the heat of solution; curve 5, ○—○—○, the electric resistance at 25°; curve 6, +—+—, the boiling-points; curve 7, ·+·—·+·—, the vapour-tensions at 100°; curve 8, —·○·—·○·—, the viscosities (times of outflow); curve 9, -•-•-•-•, the capillarity; curve 10, -ı-ı-ı-ı-ı-ı-ı-ı-, the action upon iron.

The following fact concerning a property of sulphuric acid containing about 98 per cent. H_2SO_4 is of great importance in the manufacture of sulphuric acid from SO_3 by the contact process. Knietsch found that the task of converting the SO_3 into hydrated acid cannot be accomplished by absorbing it in a series of vessels filled with water or dilute acid, although the heat of dissolution in this case is at a maximum; but acid of 97 or 98 per cent. H_2SO_4 at once and completely absorbs the SO_3, so that only one vessel is required, in which the proper concentration is maintained by continuously running in water or dilute acids and running off concentrated acid. Sackur (Zsch. f. Elektroch. 1902, p. 81) explains this by saying that at ordinary temperatures the 100 per cent. monohydrate, H_2SO_4, is slightly dissociated into H_2SO_4, H_2O+SO_3 (comp. p. 172), but in the presence of very little water (equal to 98 per cent. H_2SO_4) the partial pressure of SO_3 is at a minimum, and hence this acid has the maximum absorbing power for SO_3. Up to this point no *free* H_2O is present, but with greater dilution it is found. That these dilute acids are inferior solvents of SO_3 is explained by the fact observed by Oddo (comp. p. 163) that the true SO_3, melting at 14°, is easily dissolved in H_2SO_4, but the polymer, S_2O_6, but slowly. Now the latter is formed from SO_3 by the influence of minute quantities of water, and therefore also when SO_3 is passed into acids below 98 per cent. H_2SO_4.

The ordinary *"rectified oil of vitriol"* always contains more water than that obtainable by the highest degree of concentration or distillation. Exceptionally 98 per cent. acid is made for commercial purposes; the usual rectified O.V., formerly called 170° Twaddell, now more accurately 168° Twaddell, varies in strength from 96 down to 93 or even 92 per cent. of real monohydrate. This variation is partly caused by the fact that at the higher degree of concentration a slight difference in specific gravity corresponds to a great difference in percentage; partly by the fact that the specific gravity of commercial acids, owing to the presence of impurities, is always higher than that of the pure acid; but, apart from this, the correctness of ordinary *hydrometers* is rarely of a very high order. Still, it must be conceded that in England at least there is a possibility of making the hydrometers all alike, the basis of Twaddell's system being a plain and unmistakable one, as every degree is equal to a difference of 0·005. But matters are far worse on the Continent and in America, where Baumé's hydrometer is almost universally used; unfortunately the degrees of this instrument, as stated by various authorities, answer to very different specific gravities, and those of the instruments found in trade often show even far greater deviations. The only rational hydrometer on Baumé's system which rests on a mathematical basis, and which should therefore be always obtainable with a uniform scale, is that graduated according to the formula

$$d = \frac{144 \cdot 3}{144 \cdot 3 - n},$$

where d signifies any special density (specific gravity), and n the degree of the scale corresponding to it. (The mathematical deduction of this formula is given in the first edition of this work, pp. 20 and 21.) This scale is also generally accepted in Germany and France now. It is the only one in which the degree 66, which is that everywhere accepted for rectified O.V., comes near the real specific gravity of pure sulphuric acid of 96 per cent., or commercial acid of 94 to 95 per cent., namely 1·840. Unfortunately, apart from various other scales, Gerlach's scale is also sometimes used, although this is far lower than the "rational" scale, and, to make the confusion still greater, the American

Comparison of Baumé's Hydrometers with the Specific Gravities.

Degrees.	Rational Hydrometer, $d=\frac{144\cdot3}{144\cdot3-n}$.	Baumé's Hydrometer (Gerlach).	American Hydrometer.	Degrees.	Rational Hydrometer, $d=\frac{144\cdot3}{144\cdot3-n}$.	Baumé's Hydrometer (Gerlach).	American Hydrometer.
1	1·007	1·0068	1·005	36	1·332	1·3250	1·334
2	1·014	1·0138	1·011	37	1·345	1·3370	1·342
3	1·022	1·0208	1·023	38	1·357	1·3494	1·359
4	1·029	1·0280	1·029	39	1·370	1·3619	1·368
5	1·037	1·0353	1·036	40	1·383	1·3746	1·386
6	1·045	1·0426	1·043	41	1·397	1·3876	1·395
7	1·052	1·0501	1·050	42	1·410	1·4009	1·413
8	1·060	1·0576	1·057	43	1·424	1·4143	1·422
9	1·067	1·0653	1·064	44	1·438	1·4281	1·441
10	1·075	1·0731	1·071	45	1·453	1·4421	1·451
11	1·083	1·0810	1·086	46	1·468	1·4564	1·470
12	1·091	1·0890	1·093	47	1·483	1·4710	1·480
13	1·100	1·0972	1·100	48	1·498	1·4860	1·500
14	1·108	1·1054	1·107	49	1·514	1·5012	1·510
15	1·116	1·1138	1·114	50	1·530	1·5167	1·531
16	1·125	1·1224	1·122	51	1·540	1·5325	1·541
17	1·134	1·1310	1·136	52	1·563	1·5487	1·561
18	1·142	1·1398	1·143	53	1·580	1·5652	1·573
19	1·152	1·1487	1·150	54	1·597	1·5820	1·594
20	1·162	1·1578	1·158	55	1·615	1·5993	1·616
21	1·171	1·1670	1·172	56	1·634	1·6169	1·627
22	1·180	1·1763	1·179	57	1·652	1·6349	1·650
23	1·190	1·1858	1·186	58	1·671	1·6533	1·661
24	1·200	1·1955	1·201	59	1·691	1·6721	1·683
25	1·210	1·2053	1·208	60	1·711	1·6914	1·705
26	1·220	1·2153	1·216	61	1·732	1·7111	1·727
27	1·231	1·2254	1·231	62	1·753	1·7313	1·747
28	1·241	1·2357	1·238	63	1·774	1·7520	1·767
29	1·252	1·2462	1·254	64	1·796	1·7731	1·793
30	1·263	1·2569	1·262	65	1·819	1·7948	1·814
31	1·274	1·2677	1·269	66	1·842	1·8171	1·835
32	1·285	1·2788	1·285				
33	1·297	1·2901	1·293				
34	1·308	1·3015	1·309				
35	1·320	1·3131	1·317				

Comparison between the Degrees of Twaddell's Hydrometer and Specific Gravities.

Degrees, Tw.	Specific Gravity.	Degrees, Tw.	Specific Gravity.	Degrees, Tw.	Specific Gravity.	Degrees, Tw.	Specific Gravity.
1	1·005	44	1·220	87	1·435	130	1·650
2	1·010	45	1·225	88	1·440	131	1·655
3	1·015	46	1·230	89	1·445	132	1·660
4	1·020	47	1·235	90	1·450	133	1·665
5	1·025	48	1·240	91	1·455	134	1·670
6	1·030	49	1·245	92	1·460	135	1·675
7	1·035	50	1·250	93	1·465	136	1·680
8	1·040	51	1·255	94	1·470	137	1·685
9	1·045	52	1·260	95	1·475	138	1·690
10	1·050	53	1·265	96	1·480	139	1·695
11	1·055	54	1·270	97	1·485	140	1·700
12	1·060	55	1·275	98	1·490	141	1·705
13	1·065	56	1·280	99	1·495	142	1·710
14	1·070	57	1·285	100	1·500	143	1·715
15	1·075	58	1·290	101	1·505	144	1·720
16	1·080	59	1·295	102	1·510	145	1·725
17	1·085	60	1·300	103	1·515	146	1·730
18	1·090	61	1·305	104	1·520	147	1·735
19	1·095	62	1·310	105	1·525	148	1·740
20	1·100	63	1·315	106	1·530	149	1·745
21	1·105	64	1·320	107	1·535	150	1·750
22	1·110	65	1·325	108	1·540	151	1·755
23	1·115	66	1·330	109	1·545	152	1·760
24	1·120	67	1·335	110	1·550	153	1·765
25	1·125	68	1·340	111	1·555	154	1·770
26	1·130	69	1·345	112	1·560	155	1·775
27	1·135	70	1·350	113	1·565	156	1·780
28	1·140	71	1·355	114	1·570	157	1·785
29	1·145	72	1·360	115	1·575	158	1·790
30	1·150	73	1·365	116	1·580	159	1·795
31	1·155	74	1·370	117	1·585	160	1·800
32	1·160	75	1·375	118	1·590	161	1·805
33	1·165	76	1·380	119	1·595	162	1·810
34	1·170	77	1·385	120	1·600	163	1·815
35	1·175	78	1·390	121	1·605	164	1·820
36	1·180	79	1·395	122	1·610	165	1·825
37	1·185	80	1·400	123	1·615	166	1·830
38	1·190	81	1·405	124	1·620	167	1·835
39	1·195	82	1·410	125	1·625	168	1·840
40	1·200	83	1·415	126	1·630	169	1·845
41	1·205	84	1·420	127	1·635	170	1·850
42	1·210	85	1·425	128	1·640		
43	1·215	86	1·430	129	1·645		

manufacturers have adopted again another scale, based on the formula

$$n = 145 - \frac{145}{d}.$$

In order to clear the way as far as possible, we give herewith tables (pp. 177, 178) showing the value of a degree Baumé according to the rational scale, to Gerlach's, and to the American scale (the last is copied from A. H. Elliott, 'Chem. Trade Journal,' vol. ii. p. 183).

The percentage of *mixtures of sulphuric acid and water* is in the great majority of cases tested by the hydrometer only, and many tables have been constructed for this purpose. It would be very desirable, as Hasenclever points out (Hofmann's Report, i. p. 181), if all sulphuric-acid makers used the same reduction-tables for their calculations; for in the statements on the yield of acid, and in many other cases, frequently different tables are used; so that the working results of different factories are not always comparable with each other. This very clearly appears from the following comparative Table:—

Degrees (Baumé).	Spec. Grav. (Kolb).	Percentage of SO_4H_2 in the Vitriol according to							
		Vauquelin.	D'Arcet.	Tables of different works.				Bineau.	Kolb.
10	1·075	11·73	...	11·5	11·40	...	10·98	11·0	10·8
20	1·162	24·01	...	23·3	23·46	...	21·97	22·4	22·2
30	1·263	36·52	...	36·9	36·60	...	35·93	34·9	34·7
40	1·383	50·41	...	51·6	51·49	...	49·94	38·4	48·3
50	1·530	66·54	66·45	66·9	66·17	63·8	63·92	62·7	62·5
60	1·711	84·22	82·34	83·3	82·80	79·4	79·90	78·0	78·1
66	1·842	100·00	100·00	100·0	100·00	94·0	97·87	100·0	100·0

The totally incorrect tables of Vauquelin and D'Arcet are used, up to the present time, exclusively in the south of France.

We shall here not take any notice of those old tables, nor of those of Ure, Dalton, &c., and we refer to our first edition as to the more modern and reliable tables of Bineau and Kolb. In this place we give only the most modern and accurate results, viz., those of Lunge and Isler (Zsch. f. angew. Ch. 1890, p. 129) for the strengths up to 142° Tw., and also of Lunge and Naef (Chem. Ind. 1883, p. 37)*.

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* A very extended study of the specific gravities of sulphuric-acid solutions has been published by Pickering (Journ. of the Chem. Soc. vol. lvii. pp. 64 *et seqq.*). The reasons why I do not see any occasion for accepting Pickering's figures in lieu of my own are stated in the 'Journal of the Society of Chemical Industry,' 1890, p. 1017.

Specific Gravities of Sulphuric Acid according to Lunge & Isler and Lunge & Naef.

Spec. Grav. at $\frac{15^\circ}{4^\circ}$ (in the vacuum).	Degree Baumé.	Degree Twaddell.	100 parts by weight of chemically pure acid contain per cent.:—				1 litre of chemically pure acid contains kilograms of:—			
			SO_3.	H_2SO_4.	acid of 142° Tw.	acid of 106° Tw.	SO_3.	H_2SO_4.	acid of 142° Tw.	acid of 106° Tw.
1·000	0	0	0·07	0·09	0·12	0·14	0·001	0·001	0·001	0·001
1·005	0·7	1	0·68	0·83	1·06	1·33	0·007	0·008	0·011	0·013
1·010	1·4	2	1·28	1·57	2·01	2·51	0·013	0·016	0·020	0·025
1·015	2·1	3	1·88	2·30	2·95	3·68	0·019	0·023	0·030	0·037
1·020	2·7	4	2·47	3·03	3·88	4·85	0·025	0·031	0·040	0·050
1·025	3·4	5	3·07	3·76	4·82	6·02	0·032	0·039	0·049	0·062
1·030	4·1	6	3·67	4·49	5·78	7·18	0·038	0·046	0·059	0·074
1·035	4·7	7	4·27	5·23	6·73	8·37	0·044	0·054	0·070	0·087
1·040	5·4	8	4·87	5·96	7·64	9·54	0·051	0·062	0·079	0·099
1·045	6·0	9	5·45	6·67	8·55	10·67	0·057	0·071	0·089	0·112
1·050	6·7	10	6·02	7·37	9·44	11·79	0·063	0·077	0·099	0·124
1·055	7·4	11	6·59	8·07	10·34	12·91	0·070	0·085	0·109	0·136
1·060	8·0	12	7·16	8·77	11·24	14·03	0·076	0·093	0·119	0·149
1·065	8·7	13	7·73	9·47	12·14	15·15	0·082	0·102	0·129	0·161
1·070	9·4	14	8·32	10·19	13·05	16·30	0·089	0·109	0·140	0·174
1·075	10·0	15	8·90	10·90	13·96	17·44	0·096	0·117	0·150	0·188
1·080	10·6	16	9·47	11·60	14·87	18·56	0·103	0·125	0·161	0·201
1·085	11·2	17	10·04	12·30	15·76	19·68	0·109	0·133	0·171	0·213
1·090	11·9	18	10·60	12·99	16·65	20·78	0·116	0·142	0·181	0·227
1·095	12·4	19	11·16	13·67	17·52	21·87	0·122	0·150	0·192	0·240
1·100	13·0	20	11·71	14·35	18·39	22·96	0·129	0·158	0·202	0·253
1·105	13·6	21	12·27	15·03	19·26	24·05	0·136	0·166	0·212	0·265
1·110	14·2	22	12·82	15·71	20·13	25·14	0·143	0·175	0·223	0·279
1·115	14·9	23	13·36	16·36	20·96	26·18	0·149	0·183	0·234	0·292
1·120	15·4	24	13·89	17·01	21·80	27·22	0·156	0·191	0·245	0·305
1·125	16·0	25	14·42	17·66	22·63	28·26	0·162	0·199	0·255	0·318
1·130	16·5	26	14·95	18·31	23·47	29·30	0·169	0·207	0·265	0·331

1·135	17·1	27	15·48	18·96	24·29	30·34	0·176	0·215	0·276	0·344
1·140	17·7	28	16·01	19·61	25·13	31·38	0·183	0·223	0·287	0·358
1·145	18·3	29	16·54	20·26	25·96	32·42	0·189	0·231	0·297	0·371
1·150	18·8	30	17·07	20·91	26·79	33·46	0·196	0·239	0·308	0·385
1·155	19·3	31	17·59	21·55	27·61	34·48	0·203	0·248	0·319	0·398
1·160	19·8	32	18·11	22·19	28·43	35·50	0·210	0·257	0·330	0·412
1·165	20·3	33	18·64	22·83	29·25	36·53	0·217	0·266	0·341	0·426
1·170	20·9	34	19·16	23·47	30·07	37·55	0·224	0·275	0·352	0·439
1·175	21·4	35	19·69	24·12	30·90	38·59	0·231	0·283	0·363	0·453
1·180	22·0	36	20·21	24·76	31·73	39·62	0·238	0·292	0·374	0·467
1·185	22·5	37	20·73	25·40	32·55	40·64	0·246	0·301	0·386	0·481
1·190	23·0	38	21·26	26·04	33·37	41·66	0·253	0·310	0·397	0·496
1·195	23·5	39	21·78	26·68	34·19	42·69	0·260	0·319	0·409	0·511
1·200	24·0	40	22·30	27·32	35·01	43·71	0·268	0·328	0·420	0·525
1·205	24·5	41	22·82	27·95	35·83	44·72	0·275	0·337	0·432	0·539
1·210	25·0	42	23·33	28·58	36·66	45·73	0·282	0·346	0·444	0·553
1·215	25·5	43	23·84	29·21	37·45	46·74	0·290	0·355	0·455	0·568
1·220	26·0	44	24·36	29·84	38·23	47·74	0·297	0·364	0·466	0·583
1·225	26·4	45	24·88	30·48	39·05	48·77	0·305	0·373	0·478	0·598
1·230	26·9	46	25·39	31·11	39·86	49·78	0·312	0·382	0·490	0·612
1·235	27·4	47	25·88	31·70	40·61	50·72	0·320	0·391	0·502	0·626
1·240	27·9	48	26·35	32·28	41·37	51·65	0·327	0·400	0·513	0·640
1·245	28·4	49	26·83	32·86	42·11	52·58	0·334	0·409	0·524	0·655
1·250	28·8	50	27·29	33·43	42·84	53·49	0·341	0·418	0·535	0·669
1·255	29·3	51	27·76	34·00	43·57	54·40	0·348	0·426	0·547	0·683
1·260	29·7	52	28·22	34·57	44·30	55·31	0·356	0·435	0·558	0·697
1·265	30·2	53	28·69	35·14	45·03	56·22	0·363	0·444	0·570	0·711
1·270	30·6	54	29·15	35·71	45·76	57·14	0·370	0·454	0·581	0·725
1·275	31·1	55	29·62	36·29	46·50	58·06	0·377	0·462	0·593	0·740
1·280	31·5	56	30·10	36·87	47·24	58·99	0·385	0·472	0·605	0·755
1·285	32·0	57	30·57	37·45	47·99	59·92	0·393	0·481	0·617	0·770
1·290	32·4	58	31·04	38·03	48·73	60·85	0·400	0·490	0·629	0·785
1·295	32·8	59	31·52	38·61	49·47	61·78	0·408	0·500	0·641	0·800
1·300	33·3	60	31·99	39·19	50·21	62·70	0·416	0·510	0·653	0·815
1·305	33·7	61	32·46	39·77	50·96	63·63	0·424	0·519	0·665	0·830
1·310	34·2	62	32·94	40·35	51·71	64·56	0·432	0·529	0·677	0·846

Specific Gravities of Sulphuric Acid (continued).

Spec. Grav. at $\frac{15^\circ}{4^\circ}$ (in the vacuum).	Degree Baumé.	Degree Twaddell.	100 parts by weight of chemically pure acid contain per cent. :—				1 litre of chemically pure acid contains kilograms of:—			
			SO_3.	H_2SO_4.	acid of 142° Tw.	acid of 106° Tw.	SO_3.	H_2SO_4.	acid of 142° Tw.	acid of 106° Tw.
1·315	34·6	63	33·41	40·93	52·45	65·45	0·439	0·538	0·689	0·860
1·320	35·0	64	33·88	41·50	53·18	66·40	0·447	0·548	0·702	0·876
1·325	35·4	65	34·35	42·08	53·92	67·33	0·455	0·557	0·714	0·892
1·330	35·8	66	34·80	42·66	54·67	68·26	0·462	0·567	0·727	0·908
1·335	36·2	67	35·27	43·20	55·36	69·12	0·471	0·577	0·739	0·923
1·340	36·6	68	35·71	43·74	56·05	69·98	0·479	0·586	0·751	0·938
1·345	37·0	69	36·14	44·28	56·74	70·85	0·486	0·596	0·763	0·953
1·350	37·4	70	36·58	44·82	57·43	71·71	0·494	0·605	0·775	0·968
1·355	37·8	71	37·02	45·35	58·11	72·56	0·502	0·614	0·787	0·983
1·360	38·2	72	37·45	45·88	58·79	73·41	0·509	0·624	0·800	0·998
1·365	38·6	73	37·89	46·41	59·48	74·26	0·517	0·633	0·812	1·014
1·370	39·0	74	38·32	46·94	60·15	75·10	0·525	0·643	0·824	1·029
1·375	39·4	75	38·75	47·47	60·83	75·95	0·533	0·653	0·836	1·044
1·380	39·8	76	39·18	48·00	61·51	76·80	0·541	0·662	0·849	1·060
1·385	40·1	77	39·62	48·53	62·19	77·65	0·549	0·672	0·861	1·075
1·390	40·5	78	40·05	49·06	62·87	78·50	0·557	0·682	0·873	1·091
1·395	40·8	79	40·48	49·59	63·55	79·34	0·564	0·692	0·886	1·107
1·400	41·2	80	40·91	50·11	64·21	80·18	0·573	0·702	0·899	1·123
1·405	41·6	81	41·33	50·63	64·88	81·01	0·581	0·711	0·912	1·138
1·410	42·0	82	41·76	51·15	65·55	81·86	0·589	0·721	0·924	1·154
1·415	42·3	83	42·17	51·66	66·21	82·66	0·597	0·730	0·937	1·170
1·420	42·7	84	42·57	52·16	66·82	83·44	0·604	0·740	0·949	1·185
1·425	43·1	85	42·96	52·63	67·44	84·21	0·612	0·750	0·961	1·200
1·430	43·4	86	43·36	53·11	68·06	84·98	0·620	0·759	0·973	1·215
1·435	43·8	87	43·75	53·59	68·68	85·74	0·628	0·769	0·986	1·230
1·440	44·1	88	44·14	54·07	69·29	86·51	0·636	0·779	0·998	1·246
1·445	44·4	89	44·53	54·55	69·90	87·28	0·643	0·789	0·010	1·261
1·450	44·8	90	44·92	55·03	70·52	88·05	0·651	0·798	0·023	1·277

1·455	45·1	91	45·31	55·50	71·12	88·80	0·659	0·808	0·035	1·292
1·460	45·4	92	45·69	55·97	71·72	89·55	0·667	0·817	0·047	1·307
1·465	45·8	93	46·07	56·43	72·31	90·29	0·675	0·828	0·059	1·323
1·470	46·1	94	46·45	56·90	72·91	91·04	0·683	0·837	0·027	1·338
1·475	46·4	95	46·83	57·37	73·51	91·79	0·691	0·846	0·084	1·354
1·480	46·8	96	47·21	57·83	74·10	92·53	0·699	0·856	1·097	1·370
1·485	47·1	97	47·57	58·28	74·68	93·25	0·707	0·865	1·109	1·385
1·490	47·4	98	47·95	58·74	75·27	93·98	0·715	0·876	1·122	1·400
1·495	47·8	99	48·34	59·22	75·88	94·75	0·723	0·885	1·134	1·417
1·500	48·1	100	48·73	59·70	76·50	95·52	0·731	0·896	1·147	1·433
1·505	48·4	101	49·12	60·18	77·12	96·29	0·739	0·906	1·160	1·449
1·510	48·7	102	49·51	60·65	77·72	97·04	0·748	0·916	1·174	1·465
1·515	49·0	103	49·89	61·12	78·32	97·79	0·756	0·926	1·187	1·481
1·520	49·4	104	50·28	61·59	78·93	98·54	0·764	0·936	1·199	1·498
1·525	49·7	105	50·66	62·06	79·52	99·30	0·773	0·946	1·213	1·514
1·530	50·0	106	51·04	62·53	80·13	100·05	0·781	0·957	1·226	1·531
1·535	50·3	107	51·43	63·00	80·73	100·80	0·789	0·967	1·239	1·547
1·540	50·6	108	51·78	63·43	81·28	101·49	0·797	0·977	1·252	1·563
1·545	50·9	109	52·12	68·85	81·81	102·16	0·805	0·987	1·264	1·579
1·550	51·2	110	52·46	64·26	82·34	102·82	0·813	0·996	1·276	1·593
1·555	51·5	111	52·79	64·67	82·87	103·47	0·821	1·006	1·289	1·609
1·560	51·8	112	53·12	65·08	83·39	104·13	0·829	1·015	1·301	1·624
1·565	52·1	113	53·46	65·49	83·92	104·78	0·837	1·025	1·313	1·640
1·570	52·4	114	53·80	65·90	84·44	105·44	0·845	1·035	1·325	1·655
1·575	52·7	115	54·13	66·30	84·95	106·08	0·853	1·044	1·338	1·671
1·580	53·0	116	54·46	66·71	85·48	106·73	0·861	1·054	1·351	1·686
1·585	53·3	117	54·80	67·13	86·03	107·41	0·869	1·064	1·364	1·702
1·590	53·6	118	55·18	67·59	86·62	108·14	0·877	1·075	1·377	1·719
1·595	53·9	119	55·55	68·05	87·20	108·88	0·886	1·085	1·391	1·737
1·600	54·1	120	55·93	68·51	87·79	109·62	0·895	1·096	1·405	1·754
1·605	54·4	121	56·30	68·97	88·38	110·35	0·904	1·107	1·419	1·772
1·610	54·7	122	56·68	69·43	88·97	111·09	0·913	1·118	1·432	1·789
1·615	55·0	123	57·05	69·89	89·56	111·82	0·921	1·128	1·446	1·806
1·620	55·2	124	57·40	70·32	90·11	112·51	0·930	1·139	1·460	1·823
1·625	55·5	125	57·75	70·74	90·65	113·18	0·938	1·150	1·473	1·840
1·630	55·8	126	58·09	71·16	91·19	113·86	0·947	1·160	1·486	1·857
1·635	56·0	127	58·43	71·57	91·71	114·51	0·955	1·170	1·499	1·873
1·640	56·3	128	58·77	71·99	92·25	115·18	0·964	1·180	1·513	1·889

Specific Gravities of Sulphuric Acid (continued).

Spec. Grav. at $\frac{15^\circ}{4^\circ}$ (in the vacuum).	Degree Baumé.	Degree Twaddell.	100 parts by weight of chemically pure acid contain per cent.:—				1 litre of chemically pure acid contains kilograms of:—			
			SO_3.	H_2SO_4.	acid of 142° Tw.	acid of 106° Tw.	SO_3.	H_2SO_4.	acid of 142° Tw.	acid of 106° Tw.
1·645	56·6	129	59·10	72·40	92·77	114·84	0·972	1·191	1·526	1·905
1·650	56·9	130	59·45	72·82	93·29	116·51	0·981	1·202	1·540	1·922
1·655	57·1	131	59·78	73·23	93·81	117·17	0·989	1·212	1·553	1·939
1·660	57·4	132	60·11	73·64	94·36	117·82	0·998	1·222	1·566	1·956
1·665	57·7	133	60·46	74·07	94·92	118·51	1·007	1·233	1·580	1·973
1·670	57·9	134	60·82	74·51	95·48	119·22	1·016	1·244	1·595	1·991
1·675	58·2	135	61·20	74·97	96·07	119·95	1·025	1·256	1·609	2·009
1·680	58·4	136	61·57	75·42	96·65	120·67	1·034	1·267	1·623	2·027
1·685	58·7	137	61·93	75·86	97·21	121·38	1·043	1·278	1·638	2·046
1·690	58·9	138	62·29	76·30	97·77	122·08	1·053	1·289	1·652	2·064
1·695	59·2	139	62·64	76·73	98·32	122·77	1·062	1·301	1·667	2·082
1·700	59·5	140	63·00	77·17	98·89	123·47	1·071	1·312	1·681	2·100
1·705	59·7	141	63·35	77·60	99·44	124·16	1·080	1·323	1·696	2·117
1·710	60·0	142	63·70	78·04	100·00	124·86	1·089	1·334	1·710	2·136
1·715	60·2	143	64·07	78·48	100·56	125·57	1·099	1·346	1·725	2·154
1·720	60·4	144	64·43	78·92	101·13	126·27	1·108	1·357	1·739	2·172
1·725	60·6	145	64·78	79·36	101·69	126·98	1·118	1·369	1·754	2·191
1·730	60·9	146	65·14	79·80	102·25	127·68	1·127	1·381	1·769	2·209
1·735	61·1	147	65·50	80·24	102·82	128·38	1·136	1·392	1·784	2·228
1·740	61·4	148	65·86	80·68	103·38	129·09	1·146	1·404	1·799	2·247
1·745	61·6	149	66·22	81·12	103·95	129·79	1·156	1·416	1·814	2·265
1·750	61·8	150	66·58	81·56	104·52	130·49	1·165	1·427	1·829	2·284
1·755	62·1	151	66·94	82·00	105·08	131·20	1·175	1·439	1·845	2·303
1·760	62·3	152	67·30	82·44	105·64	131·90	1·185	1·451	1·859	2·321
1·765	62·5	153	67·65	82·88	106·21	132·61	1·194	1·463	1·874	2·340
1·770	62·8	154	68·02	83·32	106·77	133·31	1·204	1·475	1·890	2·359
1·775	63·0	155	68·49	83·90	107·51	134·24	1·216	1·489	1·908	2·381
1·780	63·2	156	68·98	84·50	108·27	135·20	1·228	1·504	1·928	2·407

1·785	63·5	157	69·47	85·10	109·05	136·16	1·240	1·519	1·947	2·432
1·790	63·7	158	69·96	85·70	109·82	137·14	1·252	1·534	1·965	2·455
1·795	64·0	159	70·45	86·30	110·58	138·08	1·265	1·549	1·983	2·479
1·800	64·2	160	70·94	86·90	111·35	139·06	1·277	1·564	2·004	2·503
1·805	64·4	161	71·50	87·60	112·25	140·16	1·291	1·581	2·026	2·530
1·810	64·6	162	72·08	88·30	113·15	141·28	1·305	1·598	2·048	2·558
1·815	64·8	163	72·69	89·05	114·11	142·48	1·319	1·621	2·071	2·587
1·820	65·0	164	73·51	90·05	115·33	144·08	1·338	1·639	2·099	2·622
1·821	...	...	73·63	90·20	115·59	144·32	1·341	1·643	2·104	2·628
1·822	65·1	...	73·80	90·40	115·84	144·64	1·345	1·647	2·110	2·635
1·823	...	...	73·96	90·60	116·10	144·96	1·348	1·651	2·116	2·643
1·824	65·2	...	74·12	90·80	116·35	145·28	1·352	1·656	2·122	2·650
1·825	...	165	74·29	91·00	116·61	145·60	1·356	1·661	2·128	2·657
1·826	65·3	...	74·49	91·25	116·93	146·00	1·360	1·666	2·135	2·666
1·827	...	...	74·69	91·50	117·25	146·40	1·364	1·671	2·142	2·675
1·828	65·4	...	74·86	91·70	117·51	146·72	1·368	1·676	2·148	2·682
1·829	...	...	75·03	91·90	117·76	147·04	1·372	1·681	2·154	2·689
1·830	...	166	75·19	92·10	118·02	147·36	1·376	1·685	2·159	2·696
1·831	65·5	...	75·35	92·30	118·27	147·68	1·380	1·690	2·165	2·704
1·832	...	...	75·53	92·52	118·56	148·03	1·384	1·695	2·172	2·711
1·833	65·6	...	75·72	92·75	118·85	148·40	1·388	1·700	2·178	2·720
1·834	...	...	75·96	93·05	119·23	148·88	1·393	1·706	2·186	2·730
1·835	65·7	167	76·27	93·43	119·72	149·49	1·400	1·713	2·196	2·743
1·836	...	...	76·57	93·80	120·19	150·08	1·406	1·722	2·207	2·755
1·837	...	...	76·90	94·20	120·71	150·72	1·412	1·730	2·217	2·769
1·838	65·8	...	77·23	94·60	121·22	151·36	1·419	1·739	2·228	2·782
1·839	...	...	77·55	95·00	121·74	152·00	1·426	1·748	2·239	2·795
1·840	65·9	168	78·04	95·60	122·51	152·96	1·436	1·759	2·254	2·814
1·8405	...	...	78·33	95·95	122·96	153·52	1·441	1·765	2·262	2·825
1·8410	...	...	79·19	97·00	124·30	155·20	1·458	1·786	2·288	2·857
1·8415	...	...	79·76	97·70	125·20	156·32	1·469	1·799	2·305	2·879
1·8410	...	...	80·16	98·20	125·84	157·12	1·476	1·808	2·317	2·893
1·8405	...	...	80·57	98·70	126·48	157·92	1·483	1·816	2·328	2·906
1·8400	...	...	80·98	99·20	127·12	158·72	1·490	1·825	2·339	2·920
1·8395	...	...	81·18	99·45	127·44	159·12	1·494	1·830	2·344	2·927
1·8390	...	...	81·39	99·70	127·76	159·52	1·497	1·834	2·349	2·933
1·8385	...	...	81·59	99·95	128·06	159·92	1·500	1·838	2·355	2·940

The specific gravities were in each case estimated at exactly 15° C. and compared with water of 4°, the weighings being reduced to the vacuum. Special notice should be taken that all older tables (including those of Bineau, Otto, and Kolb) are entirely wrong in the case of the acids of highest strength, as the maximum of specific gravity does not (as it is made to do in those tables) coincide with the greatest strength, that is, pure monohydrated sulphuric acid, H_2SO_4. The maximum it at about 98·5 per cent., and from this point the specific gravities decline to 100 per cent. H_2SO_4; above this point, that is when SO_3 is present, they instantly rise again. (Comp. Kohlrausch, Pogg. Annal. Ergänzungsband viii. p. 675; Schertel, Journ. f. prakt. Chemie, [2] xxvi. p. 246; Lunge and Naef, Chem. Ind. 1883, p. 37; and others.)

Special attention should be drawn to the point that all tables indicate the specific gravities only for *chemically pure acids*; those for commercial impure acids are always higher; we shall return to this subject further on. The accuracy of the above-given tables may be taken as ±0·05, so that the first decimal is right, but the second serves only for determining the first.

A paper by Mendelejeff (Zeitsch. f. physik. Ch. i. p. 273) on the specific gravities of mixtures of sulphuric acid and water has only theoretical interest.

A correction for any deviation of the temperature from 15° must be made, whenever the acid tested by the hydrometer is above or below that temperature. Bineau has given a small table for this purpose, which, however, is wrong for the more dilute acids. From a very large number of observations made in the Author's laboratory, a table has been constructed showing the alterations to be made in the specific gravities observed for all strengths of acid, and for all temperatures from 0° to 100°, in order to reduce them to 15° C. This table is found in Lunge and Hurter's 'Alkali-Maker's Pocketbook'; in this place we give only the average figures. For each degree above or below 15° you should add to or deduct from the specific gravity observed :—

0·0006 with acids up to 1·170
0·0007 with acids from 1·170 to 1·450
0·0008 ,, ,, 1·450 ,, 1·580
0·0009 ,, ,, 1·580 ,, 1·750
0·0010 ,, ,, 1·750 ,, 1·840

All observers agree that the solutions of sulphuric acid contain different *hydrates*. The literature of this subject is very large, and we shall here quote only the most important facts (comp. also Mendelejeff, *supra*, p. 186, and Pickering, p. 179). A sesquihydrate of sulphuric acid cannot be established as a certain chemical compound, but the *double hydrate*, $SO_4H_2 + H_2O$, is known with certainty. It crystallizes from rather more dilute acid—for instance, acid of 144° Tw. in the cold. It contains 84·48 monohydrate +15·52 water (or 68·97 anhydride +31·03 water), melts at +8° C., but, owing to superfusion, generally only solidifies below this temperature (for instance, in the depth of winter); at 205° to 210° C. it already loses 1 mol. H_2O and leaves ordinary oil of vitriol behind. The crystals form large, clear, hexagonal columns with six-pointed end-faces. Spec. grav. 1·78 to 1·79. By the crystallization of this hydrate carboys are often cracked in winter; acid of 144° Tw. and the like ought therefore only to be warehoused in places where the temperature will not sink too low, for instance below the acid-chambers. Stronger or weaker acid can be exposed to the cold of winter without any danger.

A third hydrate, $SO_4H_2 + 2H_2O$, is assumed, because, on diluting strong vitriol with water down to this point (that is, corresponding to 73·13 per cent. monohydrate, or 59 70 per cent. anhydride), the largest contraction, viz. from 100 volumes to 92·14 volumes, takes place. Bourgoin (Bull. Soc. Chem. [2] xii. p. 433) infers the same from observations on electrolyzing dilute vitriol. The density of this mixture is variously stated by different observers:—by Graham at 1·6321; by Bineau, 1·665; by Kolb, 1·652; by Jacquelain, 1·6746. According to Liebig it boils at 163° to 170°; between 193° and 199° it loses one molecule of water, and is changed into $SO_2H_2 + H_2O$ (Graham).

Pickering (Chem. News, lx. p. 68) has obtained a hydrate of the formula H_2SO_4, $4H_2O$, containing 57·66 per cent. real sulphuric acid. It fuses at −25°. By adding a little water or sulphuric acid the fusing-point is at once lowered to −70°.

The specific gravities given in all the tables refer only to *pure* acid, and cannot be accepted as quite correct for the ordinary acid of trade, which always contains impurities. Kolb has examined into this matter, and has determined the influence of the common impurities upon the density of sulphuric acid, viz. that of lead sulphate, of the oxygen compounds, of nitrogen, and of sulphurous acid. Arsenic, and perhaps iron, usually occur in too small a quantity in sulphuric acid to influence its density; but certainly there may be cases, not mentioned by Kolb, in which sulphuric acid is *strongly* contaminated with salts of iron, aluminium, sodium, &c. The iron, for instance, may come from pyrites-dust; aluminium from the packing of the Glover tower, or from the fire-clay frequently employed for stopping leaks; sodium from solutions of nitrate or sulphate of soda, which sometimes inadvertently get into the chambers.

For saturated solutions of ***sulphurous acid*** in sulphuric acid of varying density, Kolb (Bull. Soc. Ind. de Mulhouse, 1872, p. 224)* gave a table which has been proved to be incorrect by J. T. Dunn (Chem. News, xliii. p. 121, and xlv. p. 270). The latter has also shown that Kolb's figures are too low. By passing a current of pure dry SO_2 through sulphuric acid of spec. grav. 1·841 he found that this acid dissolves :—

Temperature.	Volume at 760 millim. pressure.	Spec. grav. of solution at temp. of experiment.
At 11°·1 C.	33·78 vols. SO_2	1·823
„ 16 ·1	28·86 „ „	......
„ 17 ·1	28·14 „ „	......
„ 26 ·9	19·27 „ „	1·822
„ 42 ·0	12·82 „ „	1·821
„ 50 ·9	9·47 „ „	1·818
„ 62 ·3	7·21 „ „	1·816
„ 84 ·2	4·54 „ „	1·809

Dilute acids dissolve the following quantities, at temperatures varying from 15° to 16°, reduced to 760 millim. pressure :—

Spec. grav. of sulphuric acid.	Absorbs vols. SO_2.
1·753	20·83
1·626	25·17
1·456	29·87
1·257	30·52
1·151	31·82
1·067	34·08

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* Given in our 2nd edition, p. 127.

In such quantities (up to saturation) sulphurous acid certainly never occurs in commercial vitriol ; and it is very rarely that more than traces of it are found therein, since it does not agree with the *nitrogen oxides* which are most frequently found in commercial vitriol. *Nitric acid* is, if at all, only present in extremely small quantities in the sulphuric acid of trade, and therefore does not modify its density to a sensible extent ; especially it will not be found in sulphuric acid of more than 144° Tw., except *perhaps* in the nitrous vitriol from the Gay-Lussac towers ; but even this, according to my analyses (see below), under normal conditions contains mere traces of NO_3H. *Nitric oxide* can also be neglected; neither concentrated nor diluted sulphuric acid dissolves more than mere traces of it. *Nitrous acid* certainly has a very marked effect on the apparent percentage of a sulphuric acid, according to the hydrometrical test, although only in "nitrous vitriol" such large proportions of nitrous acid occur as to influence the specific gravity of the sulphuric acid.

Kolb (*loc. cit.* and our 2nd edition, p. 129) has given a table for the specific gravities of solutions of N_2O_3 (or rather of SO_5NH, comp. below) in sulphuric acid which is useless, as it is founded upon erroneous assumptions.

R. Kisling (Chem. Ind. 1886, p. 137) has examined the effect of a percentage of *arsenic* on the specific gravity of sulphuric acid. The specific gravities of two commercial acids, A and B, were observed at 15° C. and calculated for water of 4° C. and the vacuum, in order to be comparable with Lunge and Naef's figures for pure acid (*supra*, p. 119).

A.			B.		
Spec. grav. at 15°.	SO_4H_2 per cent.	As_2O_3 per cent.	Spec. grav. at 15°.	SO_4H_2 per cent.	AS_2O_3 per cent.
1·8377	....	0·137	1·8367	93 82	0·024
1·8387	....	0·137	1·8372	93·67	0·035
1·8393	92·87	0·192	1·8373	93·12	0·028
1·8409	93·28	0·258	1·8384	93·72	0·037
1·8412	94·25	0 219	1·8386	93·96	0·037
1·8413	93·60	0·254	1·8388	94·04	0 039
1·8414	93·93	0·231	......	.....	......
1·8415	93·77	0·231	......	......	......

When comparing these results with those of Lunge and Naef, the considerable influence of the arsenious acid on the specific gravity of sulphuric acid is very apparent.

With respect to *lead sulphate*, Kolb found that, at the ordinary temperature, there were dissolved in

100	parts vitriol	of	1·841	spec. grav.	0·039	part.
100	„	„	1·793	„	0·011	„
100	„	„	1·540	„	0·003	„

In more dilute acids the lead can hardly be estimated. Nitric acid, which anyhow occurs in very small quantities, does not strongly influence the solubility of lead sulphate in sulphuric acid, nitrous acid not at all. The effect of lead sulphate on the density of vitriol can accordingly be neglected for the ordinary temperature; at most it would influence the fourth place of decimals.

Although, as we see, the impurities of ordinary sulphuric acid, leaving aside "nitrous vitriol," have very little effect on its density, still the latter, at the highest degrees of concentration, is no trustworthy means of estimating the percentage of real SO_4H_2 in the acid, even when the correction for temperature mentioned on p. 186 is applied, because at this concentration a small difference in density corresponds to a very large difference in percentage. Many factories have special hydrometers, in which the last few degrees are spread over a large area and are further subdivided; but in fact the density ought to be estimated by more accurate methods, for the hydrometers are frequently not reliable, and certainly not so unless the normal temperature for which they have been made be *exactly* observed. But any determination of density for estimating the percentage of the very strongest acids must be rejected, after what we have seen on p. 186. The acids from 96 per cent. upwards ought therefore always to be estimated alkalimetrically.

The following table of Anthon's will be of practical value. It shows in column *a* how many parts of oil of vitriol of 168° Tw. must be mixed with 100 parts water at 15° or 20° in order to obtain an acid of the specific gravity *b*.

a.	*b.*	*a.*	*b.*	*a.*	*b.*
1	1·009	130	1·456	370	1·723
2	1·015	140	1·473	380	1·727
5	1·035	150	1·490	390	1·730
10	1·060	160	1·510	400	1·733
15	1·090	170	1·530	410	1·737
20	1·113	180	1·543	420	1·740
25	1·140	190	1·556	430	1·743
30	1·165	200	1·568	440	1·746
35	1·187	210	1·580	450	1·750
40	1·210	220	1·593	460	1·754
45	1·229	230	1·606	470	1·757
50	1·248	240	1·620	480	1·760
55	1·265	250	1·630	490	1·763
60	1·280	260	1·640	500	1·766
65	1·297	270	1·648	510	1·768
70	1·312	280	1·654	520	1·770
75	1·326	290	1·667	530	1·772
80	1·340	300	1·678	540	1·774
85	1·357	310	1·689	550	1·776
90	1·372	320	1·700	560	1·777
95	1·386	330	1·705	580	1·778
100	1·398	340	1·710	590	1·780
110	1·420	350	1·714	600	1·782
120	1·438	360	1·719		

The *melting-points* of sulphuric acids of different degrees of concentration are given by Payen in a table quoted in our 2nd edition, p. 133.

A new determination by myself (Berl. Ber. 1881, p. 2649) gave the following results :—

Spec. grav. of acid at 15° C.	Freezing-point.	Melting-point.
1·671 . . .	liquid at −20° C.	liquid.
1·691 . . .	do.	do.
1·712 . . .	do.	do.
1·727 . . .	−7·5°	−7·5°
1·732 . . .	−8·5	−8·5
1·749 . . .	−0·2	+4·5
1·767	+1·6	+6·5
1·790 . . .	+4·5	+8·0
1·807 . . .	−9·0	−6·8
1·822 . . .	liquid at −20° C.	liquid.
1·840 . . .	do.	do.

Pickering (J. Chem. Soc. 1890, lvii. pp. 331 *et seq.*) has published an extensive memoir on the freezing-points of sulphuric acid and its solutions. Thilo (Journ. Soc. Chem. Ind. 1893, p. 827) gives very extended tables as to the results obtained by him in R. Pictet's laboratory. Pictet, himself, subsequently (Compt. Rend. cxix. p. 642) supplies the following table :—

Formula.	SO_4H_2 per cent.	Spec. grav.	Freezing-point.	Formula.	SO_4H_2 per cent.	Spec. grav.	Freezing-point.
H_2SO_4	100·00	1·842	+10°	H_2SO_4+ 15 H_2O	26·63	1·196	− 34°
„ $+H_2O$	84·48	1·777	+ 3	„ 16 „	25·39	1·187	− 26·5
„ $2H_2O$	73·08	1·650	−70	„ 18 „	23·22	1·170	− 19
„ 4 „	57·65	1·476	−40	„ 20 „	21·40	1·157	− 17
„ 6 „	47·57	1·376	−50	„ 25 „	17·88	1·129	− 8·5
„ 8 „	40·50	1·311	−65	„ 50 „	9·82	1·067	− 3·5
„ 10 „	35·25	1·268	−88	„ 75 „	6·77	1·045	0
„ 11 „	33·11	1·249	−75	„ 100 „	5·16	1·032	+ 2·5
„ 12 „	31·21	1·233	−55	„ 300 „	1·78	1·007	+ 4·5
„ 13 „	29·52	1·219	−45	„ 1000 „	0·54	1·001	+ 0·5
„ 14 „	28·00	1·207	−40				

Knietsch (Ber. 1901, p. 4100) gives the following table of the melting-points of sulphuric acid, ordinary and fuming, from 1 per cent. to 100 per cent. SO_3, which I have supplemented by adding the corresponding percentages of H_2SO_4. By "melting-point" he understands the temperature at which the cooled acids in which crystals had commenced to form remained constant when the vessel was taken out of the cooling medium during the process of solidification. In a set of curves appended to the original (comp. fig. 39, p. 174) he also shows the temperatures at which the first crystals form and those at which, on cautiously heating, the last crystals were liquefied. The curves show a decided maximum near the point H_2SO_4,H_2O, a minimum at the point $2H_2SO_4,H_2O$, a maximum (nearly coinciding with the first) at the point H_2SO_4, a minimum at $4H_2SO_4,SO_3$, a strong maximum at H_2SO_4,SO_3 (=pyrosulphuric acid), a minimum at $H_2SO_4,2SO_3$, and the highest maximum for SO_3 in the polymerized state.

SO_3 p. cent.	H_2SO_4 p. cent.	Melting-point °C.	SO_3 p. cent.	H_2SO_4 p. cent.	Melting-point °C.	SO_3 p. cent.	Melting-point °C.
1	1·22	− 0·6	...	...	below −40°	82	+ 8·2
2	2·45	− 1·0	...	...		83	− 0·8
3	3·67	− 1·7	61	74·72	−40	84	− 9·2
4	4·90	− 2·0	62	75·95	−20	85	−11·0
5	6·12	− 2·7	63	77·17	−11·5	86	− 2·2
6	7·35	− 3·6	64	78·40	− 4·8	87	+13·5
7	8·57	− 4·4	65	79·62	− 4·2	88	+26·0
8	9·80	− 5·3	66	80·85	+ 1·2	89	+34·2
9	11·02	− 6·0	67	82·07	+ 8·0	90	+34·2
10	12·25	− 6·7	68	83·39	+ 8·0	91	+25·8
11	13·47	− 7·2	69	84·52	+ 7·0	92	+14·2
12	14·70	− 7·9	70	85·75	+ 4·0	93	+ 0·8
13	15·92	− 8·2	71	86·97	− 1·0	94	+ 4·5
14	17·15	− 9·0	72	88·20	− 7·2	95	+14.8
15	18·37	− 9·3	73	89·42	−16·2	96	+20·3
16	19·60	− 9·8	74	90·65	−25·0	97	+29·2
17	20·82	−11·4	75	91·87	−34·0	98	+33·8
18	22·05	−13·2	76	93·10	−32·0	99	+36·0
19	23·27	−15·2	77	94·83 66° B.	−23·2	100	+40·0
20	24·50	−17·1	78	95·05	−16·5		
21	25·72	−22·5	79	96·77	− 5·2		
22	26·95	−31·0	80	98·00	+ 3·0		
23	28·17	−40·1	81	99·25	+ 7·0		
			81·63	100·00	+10·0		

On *boiling* dilute sulphuric acid, at first nothing but aqueous vapour escapes; according to Graham, acid vapour is mixed with the steam only when no more than 2 molecules of water are present to 1 of SO_3—that is, with a percentage of 84·48 SO_4H_2 or a specific gravity of 1·78. After several discussions about the loss of sulphuric acid in concentrating it, by myself, Bode, Walter, &c., it may be assumed that in manufacturing practice no sensible loss of acid takes place by real *volatilization* up to a strength of 144° or even of 152° Tw.; but from violently boiling acid there is always a little acid carried away mechanically in the shape of small drops, especially in pans fired from the top and also in the Glover tower, or in a "vesicular state." When the evaporation up to that point takes place quietly at a moderate heat, there is probably no loss of acid at all.

The *boiling-point* of sulphuric monohydrate is stated by Marignac =338°, by Pfaundler =317°. The boiling-points of sulphuric acid containing water were examined by Dalton in the beginning of this century. His table, which was obviously wrong, has been replaced by another, founded upon the author's investigations (Berl. Ber. xi. p. 370).

TABLE I.

Specific gravity.	Temperature. ° C.	Spec. grav. reduced to 15° C.	Percentage of SO_4H_2.	Boiling-point. ° C.	Barometer reduced to 0°: millims.
1·8380	17	1·8400	95·3	297	718·8
1·8325	16·5	1·8334	92·8	280	723·9
1·8240	15·5	1·8242	90·4	264	720·6
1·8130	16	1·8140	88·7	257	726·0
1·7985	15·5	1·7990	86·6	241·5	720·1
1·7800	15	1·7800	84·3	228	720·5
1·7545	16	1·7554	81·8	218	726·0
1·7400	15	1·7400	80·6	209	720·6
1·7185	17	1·7203	78·9	203·5	725·9
1·7010	18	1·7037	77·5	197	725·2
1·6750	19	1·6786	75·3	183·5	725·2
1·6590	16	1·6599	73·9	180	725·2
1·6310	17	1·6328	71·5	173	725·2
1·6055	17	1·6072	69·5	169	730·1
1·5825	15	1·5825	67·2	160	728·8
1·5600	17	1·5617	65·4	158·5	730·1
1·5420	17	1·5437	64·3	151·5	730·1
1·4935	18	1·4960	59·4	143	730·1
1·4620	17	1·4635	56·4	133	730·1
1·4000	17	1·4015	50·3	124	730·1
1·3540	17	1·3554	45·3	118·5	730·1
1·3180	17	1·3194	41·5	115	730·1
1·2620	17	1·2633	34·7	110	732·9
1·2030	17	1·2042	27·6	107	732·9
1·1120	17	1·1128	15·8	103·5	732·9
1·0575	17	1·0580	8·5	101·5	735·0

TABLE II.

(Calculated by graphical interpolation.)

Percent. SO_4H_2.	Boiling-point.	Percent. SO_4H_2.	Boiling-point.	Percent. SO_4H_2.	Boiling-point.	Percent. SO_4H_2.	Boiling-point.
5	101°	45	118°·5	70	170°	86	238°·5
10	102	50	124	72	174·5	88	251·5
15	103·5	53	128·5	74	180·5	90	262·5
20	105	56	133	76	189	91	268
25	106·5	60	141·5	78	199	92	274·5
30	108	62·5	147	80	207	93	281·5
35	110	65	153·5	82	218·5	94	288·5
40	114	67·5	161	84	227	95	295

The *tension of aqueous vapour* in sulphuric-acid solutions of various strengths was determined by Regnault in 1845 (Ann. de Chim. [3] xv. p. 179) for temperatures from 5° to 35° C. We here give his table (for every other degree), adding to the hydrates quoted by him the percentage composition and specific gravities. We also subjoin Sorel's table (p. 196), computed for a wider interval of temperatures, better suited for the wants of sulphuric-acid manufacture. The tensions are stated in millimetres of mercurial pressure.

Regnault's Table of the Aqueous-Vapour Tensions of Dilute Sulphuric Acid.

°C.	H_2SO_4 $+H_2O$ 84·5%. 1·780.	H_2SO_4 $+2H_2O$ 73·1%. 1·654.	H_2SO_4 $+3H_2O$ 64·5%. 1·554.	H_2SO_4 $+4H_2O$ 57·6%. 1·477.	H_2SO_4 $+5H_2O$ 52·1 %. 1·420	H_2SO_4 $+7H_2O$ 43·7 %. 1·340.	H_2SO_4 $+9H_2O$ 37·7 %. 1·287.	H_2SO_4 $+11H_2O$ 33·1 %. 1·247.	H_2SO_4 $+17H_2O$ 24·3 %. 1·176.
5	0·105	0·388	0·861	1·294	2·137	3·168	4·120	4·428	5·478
7	0·108	0·430	0·985	1·510	2·464	3·643	4·728	5·164	6·300
9	0·112	0·476	1·125	1·753	2·829	4·176	5·408	5·980	7·216
11	0·118	0·527	1·280	2·025	3·240	4·773	6·166	6·883	8·237
13	0·124	0·586	1·454	2·331	3·699	5·443	7·013	7·885	9·374
15	0·131	0·651	1·648	2·674	4·215	6·194	7·958	8·995	10·641
17	0·139	0·725	1·865	3·059	4·793	7·036	9·014	10·222	12·054
19	0·149	0·808	2·108	3·492	5·440	7·980	10·191	11·583	13·628
21	0·159	0·901	2·380	3·977	6·166	9·039	11·506	13·090	15·383
23	0·171	1·006	2·684	4·523	6·979	10·226	12·974	14·760	17·338
25	0·184	1·125	3·024	5·135	7·892	11·557	14·613	16·610	19·516
27	0·199	1·258	3·405	5·822	8·914	13·050	16·443	18·659	21·944
29	0·216	1·408	3·830	6·594	10·060	14·723	18·485	20·929	24·650
31	0·235	1·557	4·305	7·459	11·345	16·600	20·765	23·443	27·666
33	0·256	1·767	4·838	8·432	12·785	18·704	23·311	26·228	31·025
35	0·280	1·981	5·432	9·524	14·400	21·063	26·152	29·314	34·770

Knietsch (*l. c.* p. 4111) has also determined the vapour-tensions of sulphuric acid, both ordinary and fuming, at various temperatures up to 100° C. As may be imagined, the aqueous-vapour pressures decline rapidly with the concentration of the ordinary acid, and for acids from 90 to 98·6 per cent. they are=0 even at 100°. From this point the vapour-tension, now of course produced by SO_3, rises very rapidly, as is shown by the following table (p. 197), where the pressure of $\frac{3}{4}$ vol. fuming acid + $\frac{1}{4}$ vol. air is expressed in atmospheres.

Tension of Aqueous Vapour in mixtures of Sulphuric Acid and Water (Sorel).

Spec. grav. of Acid.	Approx. degree Twaddell.	Per-cent. of H_2SO_4.	Temperatures (° C.).																	
			10°	15°	20°	25°	30°	35°	40°	45°	50°	55°	60°	65°	70°	75°	80°	85°	90°	95°
			mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
1·342	68½	44	4·4	6·1	8·5	11·5	15·5	20·9	28·1	37·4	48·3	......	......	......	......	......	......	......	......	......
1·361	72	46	4·0	5·5	7·7	10·5	14·5	19·7	26·3	33·6	44·4	59·6	76·5	96·4	......	.....	......	......	......	......
1·380	76	48	3·7	5·0	7·1	9·6	13·4	18·1	23·9	30·5	40·1	53·5	69·0	86·8	107·2	132·1	......	......	......	......
1·399	80	50	3·3	4·5	6·5	8·8	12·0	16·4	21·4	27·4	35·9	47·4	61·3	77·0	95·6	118·1	152·0	192·6	236·7	......
1·418	83½	52	3·0	4·0	5·8	7·9	10·9	14·5	18·9	24·1	31·5	41·5	54·0	67·9	84·5	104·5	131·2	166·5	207·9	251·5
1·439	88	54	2·6	3·6	5·0	7·0	9·5	12·5	16·5	21·3	27·8	36·2	47·2	59·9	74·8	92·6	116·1	146·8	183·5	222·0
1·459	92	56	2·2	3·1	4·3	6·0	8·1	11·0	14·2	18·5	24·1	31·0	41·6	51·6	65·0	80·6	100·9	128·2	160·0	195·0
1·480	96	58	1·9	2·6	3·5	5·1	7·2	9·1	12·0	15·8	20·4	26·1	34·5	44·0	55·4	68·4	86·2	110·6	138·5	169·5
1·502	100½	60	1·6	2·1	3·0	4·3	6·1	7·5	10·0	13·0	16·9	21·6	28·7	36·7	46·1	56·7	72·3	94·0	118·7	146·0
1·525	105	62	1·4	1·8	2·6	3·6	5·0	6·5	8·1	10·5	13·9	17·7	23·0	30·0	37·7	46·2	59·7	78·2	100·7	125·0
1·547	109½	64	1·2	1·6	2·2	3·0	4·0	5·5	6·5	8·2	10·9	14·0	18·7	23·9	30·3	37·4	48·0	63·8	83·7	105·0
1·569	114	66	1·1	1·4	1·8	2·5	3·5	4·5	5·4	6·5	8·9	11·5	15·2	19·1	24·2	30·3	39·0	52·5	70·0	88·0
1·592	118½	68	0·9	1·2	1·5	2·1	3·0	3·8	4·5	5·4	7·2	9·5	12·3	15·4	19·4	24·4	31·4	42·5	56·0	72·0
1·615	123	70	0·8	1·0	1·3	1·8	2·5	3·3	3·8	4·4	5·9	7·5	9·5	12·1	15·5	19·8	25·5	33·9	44·4	57·0
1·638	127½	72	0·7	0·8	1·0	1·4	2·0	2·8	3·2	3·6	4·8	6·0	7·5	9·5	12·0	15·4	20·0	26·2	33·7	43·4
1·662	132½	74	0·5	0·6	0·6	1·2	1·7	2·1	2·6	3·1	3·9	4·9	6·0	7·5	9·5	12·1	15·4	19·5	24·5	31·5
1·687	137½	76	0·4	0·4	0·5	1·0	1·4	1·8	2·1	2·5	3·0	4·0	4·8	5·9	7·5	9·5	11·8	15·0	18·5	22·0
1·710	142	78	0·3	0·3	0·4	0·8	1·1	1·4	1·7	2·1	2·4	3·0	3·5	4·0	5·7	7·0	8·5	10·5	13·0	15·8
1·733	146½	80	0·2	0·2	0·3	0·6	0·8	1·1	1·3	1·6	1·9	2·4	2·9	3·3	4·1	5·0	6·2	7·5	9·3	11·0
1·755	151	82	0·1	0·1	0·2	0·4	0·5	0·5	0·9	1·1	1·4	1·7	2·0	2·3	2·7	3·2	3·9	4·7	5·6	6·8

Temp. ° C.	SO_3 30 p. c. atm.	SO_3 40 p. c. atm.	SO_3 50 p. c. atm.	SO_3 60 p. c. atm.	SO_3 70 p. c. atm.	SO_3 80 p. c. atm.	SO_3 100 p. c. atm.
35	...	...	...	...	...	0·150	0·400
40	...	0·075	...	0·225	0·375	0·500	0·650
45	0·050	0·125	...	0·350	0·575	0·650	0·875
50	0·100	0·175	0·350	0·525	0·775	0·875	1·200
55	0·140	0·225	0·450	0·675	1·025	1·200	1·600
60	0·200	0·275	0·550	0·825	1·400	1·500	1·850
65	0·225	0·350	0·700	1·025	1·650	1·900	2·250
70	0·275	0·400	0·825	1·275	2·050	2·300	2·725
75	0·340	0·475	1·000	1·570	2·525	2·800	3·300
80	0·400	0·575	1·150	1·850	3·100	3·500	4·000
85	0·450	0·675	1·400	2·150	3·700	4·175	4·900
90	0·530	0·825	1·700	2·575	4·400	5·050	5·900
95	0·625	0·950	2·050	3·150	5·200	6·000	...
100	0·730	1·000	2·400	3·700	6·000	...	...

The *specific heat* of monohydrated sulphuric acid at 16°–20° C. is 0·3315 (water = 1). Marignac states the specific heat of acid diluted with water as follows:—

H_2SO_4 + 5 aq. = 0·5764
„ 10 „ 0·7212
„ 15 „ 0·7919
„ 25 „ 0·8537
„ 50 „ 0·9155
„ 100 „ 0·9545
„ 200 „ 0·9747
„ 400 „ 0·9878

The following table, by Bode, is more convenient for practical use (Zeitschr. f. angew. Chem. 1889, p. 244):—

Spec. grav.	Spec. heat.	Spec. grav.	Spec. heat.
1·842	0·3315	1·020	0·67
1·774	0·38	1·263	0·73
1·711	0·41	1·210	0·78
1·615	0·45	1·162	0·82
1·530	0·49	1·116	0·87
1·442	0·55	1·075	0·90
1·383	0·60	1·037	0·95

Comp. also Pickering (J. Chem. Soc. lvii. p. 90).

Knietsch (Berl. Ber. 1901, p. 4102) gives the specific heats of acids of higher concentration and fuming acids, up to 100 per cent. anhydride. The curve (fig. 39, p. 174) falls continuously with the concentration, till 20 per cent. SO_3 is reached; it then rises again, and at 100 per cent. SO_3 reaches the considerable amount of 0·77. The principal points are :—

Total SO_3.	Free SO_3.	Spec. heat.	Total SO_3.	Free SO_3.	Spec. heat.
80	...	0·3574	92	56·45	0·400
82	2·0	0·345	94	67·34	0·455
84	12·89	0·340	96	78·23	0·535
86	23·78	0·340	98	89·12	0·650
88	34·67	0·350	100	100	0·770
90	45·56	0·360			

Chemical behaviour of Sulphuric Acid.

On mixing oil of vitriol with water a considerable rise of temperature takes place, water being chemically fixed by the formation of certain hydrates, as described above. Besides, on mixing concentrated acid with water, as already mentioned, a not inconsiderable contraction takes place, which must equally lead to an evolution of heat. But on mixing strong sulphuric acid with snow excessive cold is produced by the heat becoming latent on the liquefaction of snow, which considerably exceeds that becoming free in consequence of the chemical combination. This cold, however, is only produced when the proportion between acid and ice does not exceed certain limits: for 1 part of sulphuric acid there must be 1¼ part of snow present; with less snow there is a rise of temperature.

Even when more strongly diluted much heat is liberated. Many observers have worked upon this subject; but we quote here only a few. Thomsen (Deutsch. chem. Ges. Ber. iii. p. 496) states that one gram-molecule (that is 98 grams) H_2SO_4 gives the following amounts of heat when combining with x molecules of water :—

x.		
1	6272	metrical heat-units.
2	9364	„ „
3	11108	„ „
5	13082	„ „
9	14940	„ „
19	16248	„ „
49	16676	„ „
99	16850	„ „
199	17056	„ „
499	17304	„ „
799	17632	„ „
1599	17848	„ „

Somewhat higher results were obtained by Pickering (J. Chem. Soc. lvii. p. 94).

Knietsch (Berl. Ber. 1901, p. 4103) gives the following figures of the heat of dissolution, found both in the laboratory and by large scale experiments with 400 kgs. water (for the values of fuming acid, see p. 170):—

SO_3 per cent.	H_2SO_4 per cent.	Calories.	SO_3 per cent.	H_2SO_4 per cent.	Calories.
50	61·25	39	67	82·08	93
51	62·48	41	68	83·30	98
52	63·70	44	69	84·53	103
53	64·93	46·5	70	85·75	108
54	66·15	49	71	86·98	113
55	67·38	51·5	72	88·20	119
56	68·60	54	73	89·43	126
57	69·83	57	74	90·65	133
58	71·05	59·5	75	91·88	139
59	72·28	62	76	93·10	146
60	73·50	65	77	94·33	152
61	74·73	68	78	95·55	160
62	75·95	72	79	96·78	168
63	77·18	75	80	98·00	178
64	78·40	79	81	99·23	188
65	79·63	83·5	81·63	100·00	193
66	80·85	88			

The curve both for ordinary and fuming acid runs on quite steadily, without any breaks, so that the formation of the different hydrates evidently does not cause any special heat-action.

On account of this considerable evolution of heat, concentrated sulphuric acid and water must always be mixed with care: the water ought never to be poured into the acid, but the acid run in a thin jet into the water with constant stirring. On a sudden mixture, so much heat is liberated at once that the acid may be raised to the boiling-point and splash about; and glass vessels are easily cracked thereby.

The affinity of sulphuric acid for water is also proved by its great hygroscopicity. Concentrated sulphuric acid is one of the best means for drying gases; and it is not only used in this way for innumerable scientific, but also for some technical purposes—for instance, in the manufacture of chlorine by Deacon's process, where the gaseous mixture, having been deprived of its hydrochloric acid by water, is passed through a coke-tower fed with sulphuric acid, in order to be deprived of its moisture. In the same way, chlorine gas is dried for the process of utilizing tinned scrap-iron by treatment with chlorine, which in the dry state does not act upon iron, but gives with tin anhydrous tin tetrachloride.

Concentrated sulphuric acid acts also upon liquid and solid bodies by depriving them of water or even splitting off the elements of the same if the substance only contains the latter, but no readily formed water. Upon this action, too, a host of scientific and technical applications of sulphuric acid are founded. In this case frequently the so-called *sulphonic acids* are formed, generally compounds easily lending themselves to further reactions. Instances of this are:—the formation of ether by the splitting-up of sulphuric acid, with the intermediate formation of sulphovinic acid; that of ethylene on the further splitting-off of water; the preparation of nitrobenzene, picric acid, nitronaphthalene; the manufacture of resorcine and alizarine by the alkaline fusion of the sulphuric acids of benzene and anthraquinone; and many other cases.

The charring of many organic substances, such as wood, sugar, &c., by contact with strong sulphuric acid, proceeds from the same source. Necessarily this acid, in its concentrated form, must have an extremely prejudicial effect on the animal body. The remedy usually applied, viz. burnt magnesia, cannot do much good when the epithelium of the œsophagus and the stomach are once destroyed.

The affinity of concentrated sulphuric acid for water is also shown by the fact that it easily runs over, when kept in open vessels, by attracting moisture from the air — a fact to be remembered in the case of balances &c.

Decompositions of Sulphuric Acid.—Some of these have been mentioned already—for instance, that into anhydride and water by evaporation. The mixed vapour, on account of the unequal velocity of diffusion of the two vapours, can be separated to a great extent into its two constituents, so that at 520° C., in an hour, a residue of 60 per cent. monohydrate and 40 per cent. anhydride, at 445° C. 75 per cent. monohydrate and 25 per cent. anhydride was obtained (Wanklyn and Robinson, Proc. Roy. Soc. xii. p. 507). Perhaps a process for preparing fuming acid can be founded upon this fact. Even far below the boiling-point the dissociation begins in the liquid acid. It has been pointed out that already at 30° to 40° C. the hydrate begins to give off vapours of anhydride (Marignac), which fact has been confirmed by the exact researches of Dittmar (Chem. Soc. Journ. [2] vii. p. 446) and Pfaundler & Polt (Zeitschr. f. Chemie, xiii. p. 66).

A more thorough decomposition into sulphur dioxide, oxygen, and water takes place on conducting the vapour of sulphuric acid through porcelain or platinum tubes filled with bits of porcelain and heated to a bright red heat. This mode of decomposition has been recommended by Deville and Debray as a "cheap" plan for making oxygen; but it does not seem to have answered, owing to the insufficient sale of sulphurous acid or its salts; it was expected to play a great part in the manufacture of anhydride by Winkler's process, but even for this purpose it has not been found economical.

On heating with charcoal to 100° or up to 150° C., sulphuric acid yields carbon dioxide and sulphur dioxide; on boiling with phosphorus, sulphur; on boiling with sulphur, sulphur dioxide; by the action of the electric current, hydrogen, oxygen, sulphur, &c. (in dilute sulphuric acid the electric current merely causes the decomposition of water).

Sulphuric acid at temperatures below its boiling-point behaves as the strongest of all acids, and expels all other acids from their salts when the solubilities &c. allow this; but, inversely, sodium sulphate is also decomposed by hydrochloric acid. In fact, the "avidity" of hydrochloric and nitric acid at ordinary temperatures much exceeds that of sulphuric acid. Boussingault (Ann. Chim. Phys. [5] ii. p. 120) has shown that dry hydrochloric-acid gas at a red heat decomposes the sulphates of sodium, potassium, barium, strontium, and calcium (see further on). More refractory acids expel sulphuric acid at higher temperatures—for instance, boric acid, silica, and phosphoric acid.

With the bases sulphuric acid forms two principal series of salts, viz. acid ones, of the formula $SO_2\langle{}^{OH}_{OM}$, and neutral ones, of the formula $SO_2\langle{}^{OM}_{OM}$. Very frequently it also occurs in basic salts, rarely in hyperacid salts.

The technical applications of sulphuric acid to a great extent rest on its great affinity to all bases. Of its salts the acid and neutral ones are soluble in water, excepting the neutral salts of barium, strontium, lead, silver, and mercury (in the state of protoxide), which are little or not at all soluble in water and dilute acids. Calcium sulphate is sparingly soluble in water. Most sulphates are insoluble in alcohol. The *basic* sulphates are mostly insoluble in water, but soluble in acids. The sulphates incline very much towards the formation of double salts, of which those are called *alums* which contain a combination of univalent and trivalent (corresponding to a double atom of quadrivalent) metals.

The neutral salts of the alkali-metals, of calcium, magnesium, silver, manganese, and ferrosum, the latter only if entirely free from acid and peroxide (a condition very rarely realized), do not redden blue litmus-paper, whilst all other soluble sulphates do this.

On *heating* to a red heat, only the neutral sulphates of the alkalies, of the alkaline earths, and of lead remain unchanged. At a still higher temperature (that of melting iron) the two latter classes are also decomposed, but the alkaline sulphates are volatilized without a change. Even zinc sulphate and manganous sulphate are not easily decomposed. This explains the difficulty of completely converting blende into oxide of zinc.

On roasting, the decomposable sulphates yield metallic oxides, sulphur dioxide, and oxygen. They are much more easily split up on heating by certain additions, such as coal, iron, &c.

On the *metals* sulphuric acid acts in a very different way. The water-decomposing metals in the cold yield nothing but hydrogen with it; at high temperatures even zinc and iron already yield sulphurous acid; and zinc, if certain conditions are observed, can even yield sulphuretted hydrogen (Fordos and Gélis).

Most of the heavy metals do not act upon sulphuric acid in the cold and in a dilute state (they yield sulphur dioxide only on being heated with *concentrated* acid), such as arsenic, antimony, bismuth, tin, lead, copper, mercury, silver (sulphates being formed at the same time); gold, platinum, iridium, and rhodium do not act on sulphuric acid at any temperature.

While *pure* sulphuric acid has hardly any action whatever on *platinum*, even at its boiling-point, some action is exercised by the impurities never absent from commercial acid. Impure platinum may also be acted upon to some extent, but the action on gold is *nil*. We shall go into this subject when treating of the concentration of sulphuric acid in platinum vessels.

The behaviour of *cast-iron* towards sulphuric acid is of great technical importance. It has been known for many years past that concentrated oil of vitriol acts very little indeed upon cast-iron, whether hot or cold, provided the access of air is excluded, the moisture from which would dilute the acid and cause it to act more strongly. It was, however, at first considered an extremely bold step when Lancashire alkali-makers began to decompose common salt with sulphuric acid in cast-iron pots, as is explained in the Chapter treating of the manufacture of saltcake.

Since that period manufacturers have become much bolder, and for many years past cast-iron vessels have been employed for "parting" alloys of silver and gold by boiling sulphuric acid, for making nitrobenzene and analogous products by a mixture of strong sulphuric and nitric acid, and innumerable other purposes where strong acids have to be manipulated either hot or cold, even for the last concentration of sulphuric acid itself. Dilute sulphuric acid, if the dilution be not too strong, acts very little on cast-iron in the cold or at a gentle heat, if air be excluded; it can hence be employed for "acid eggs," in which chamber-acid is forced up, in lieu of pumps, and similar purposes.

It is usually assumed that some descriptions of cast-iron resist the attack of acids more than others. This point, together with some others of importance, has been the subject of experiments made in my laboratory (Chem. Industrie, 1886, p. 74) *.

These experiments lead to the following conclusions:—

(1) At the ordinary temperature all acids down to 106° Tw. act very little on all descriptions of cast-iron.

(2) At 100° C. the action is much stronger. It is least in the

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* A full report is also given in the second edition of this book, p. 141 to p. 143.

case of acid of 168° Tw., 1½ times stronger with acid 142° Tw., and 3 times stronger with acid 106° Tw.

(3) At the boiling-point the differences are far more pronounced. Acid of 168° Tw. acts very little even then, both in the pure state, or as commercial acid (containing a little N_2O_3), or when containing a little SO_2. But acid of 142° Tw. acts 14 times stronger at 200° than the same acid at 100° C., and 20 times stronger than acid of 168° Tw. At 285° C. commercial acid of 142° Tw. does not act very differently from pure acid of the same strength. Acid of 106° Tw. at its boiling-point (=147° C.) acts less than acid of 142° Tw. at 200° C., but still four times as much as acid of 168° Tw. at 295° C. There is no difference between pure and commercial acid in this case.

(4) The differences between various mixtures of cast-iron are of no importance against acid of 168° Tw. in all cases, and against the weaker acids at 20° and 100° C. But the latter acids at their boiling-point act decidedly less on charcoal-pig and on chilled cast-iron than on all other kinds. A difference between hot and cold casting could not be found. The strongest attack was made on Scotch pig and on mixtures containing such.

In another series of tests we examined the action of *monohydrated sulphuric acid* on various metals, both on standing 6 days at 20° and on heating 2 hours to 100° C., always with exclusion of air. The loss of weight was :—

	Loss per cent.		Loss in grams per square centimetre of surface.	
	6 days at 20° C.	2 hours at 100° C.	6 days at 20° C.	2 hours at 100° C.
Cast-iron.........	0·041	0·071	0·062	0·015
Wrought-iron...	0·175	0·313	0·056	0·095
Copper	2·630	excessive	1·115	excessive
Lead	3·480	3·650	1·790	1·847

Wrought-iron is much more acted upon than cast-iron by weaker acids, but at the ordinary temperature it resists the action of strong sulphuric acid down to 140° Tw., and probably even a little below that strength. Where, however, through the action of moist atmospheric air, the acid gets more diluted, a very strong action sets in. Hence the wrought-iron vessels in which sulphuric acid is now very generally carried must be protected inside against any access of air when empty; and at the manholes &c., where temporary access of air is unavoidable, they are best protected by a sheet of lead.

Knietsch (Ber. 1901, p. 4109) gives the following table respecting the action of sulphuric acid (ordinary and fuming) of various strengths on cast-iron, mild steel ("Flusseisen"), and puddled iron. The cast-iron contained 2·787 per cent. graphite and 3·55 per cent. total carbon, the mild steel 0·115 per cent. carbon and the puddled iron 0·076 per cent. The figures denote the loss of the metal per superficial metre an hour in grams, after treating with acid for 72 hours at 18°–20° C., with exclusion of air.

H_2SO_4 per cent.	SO_3 per cent.	Cast-iron.	Mild steel.	Puddled iron.
48·8	39·9	0·2177	...	...
61·2	50·0	0·1510	...	0·3032
67·7	55·3	0·0847	...	0·0789
73·4	59·9	0·0662	...	0·0623
79·7	65·0	0·1560	...	0·1159
83·7	68·4	0·1388	...	0·1052
85·1	69·5	0·1306	...	0·1034
88·2	72·0	0·1636	...	0·1417
90·6	73·9	0·1760	...	0·1339
92·0	75·2	0·0933	...	0·1040
93·0	75·9	0·0736	0·0987	0·0855
94·3	77·0	0·0723	0·0987	0·0708
95·4	77·9	0·1274	0·0933	0·1209
96·8	79·0	0·1013	0·0815	0·0988
98·4	80·3	0·0681	0·0533	0·0655
98·7	80·6	0·0589	0·0509	0·0570
99·2	81·0	0·0568	0·0418	0·0504
99·30	81·07	0·057	0·042	0·050
99·50	81·25	0·060	0·038	0·049
99·77	81·45	0·066	0·042	0·049
100·00	81·63	0·087	0·088	0·076
total SO_3	free SO_3			
81·8	0·91	0·201	0·393	0·323
82·02	2·00	0·190	0·285	0·514
82·28	3·64	0·132	0·441	0·687
82·54	4·73	0·154	0·956	1·075
82·80	7·45	0·151	0·566	1·321
83·50	10·17	0·079	0·758	1·540
84·20	12·89	0·270	1·024	0·892
84·62	16·16	0·271	1·400	0·758
85·05	18·34	0·076	1·988	1·530
86·00	23·78	0·070	0·245	0·471
88·24	34·67	0·043	0·033	0·053
90·07	45·56	0·040	0·018	0·019

Knietsch (*l. c.* p. 4090) makes the following further remarks on this subject. Whereas ***cast-iron*** vessels are very suitable for the manufacture of hydrated sulphuric acid, this is not the case for fuming acids,' for these, although they corrode the metal but slightly, cause it to crack, sometimes quite suddenly, with a loud report. Evidently the fuming acid penetrates into the pores of the metal, where it is reduced to SO_2 and H_2S, with formation of CO_2 from the carbon of the cast-iron—all of them gases with somewhat low critical temperatures which produce high tensions in the interior of the metal.

Wrought-iron (and zinc) is somewhat strongly acted upon by fuming acids up to 27 per cent. SO_3; this is explained by the increase of electric conductivity, apparent from the curve No. 5, fig. 39, p. 174. We notice that the minimum lies at 100 per cent. H_2SO_4: then the conductivity rises sharply, the maximum being at 10 to 15 per cent. free SO_3, whereupon it sinks just as rapidly to a minimum. At 27 per cent. free SO_3, wrought-iron is again entirely passive, and apparatus made of it may serve for many years for the manufacture of high-strength fuming acids.

The action of sulphuric acid on lead has been the subject of many experiments. Calvert and Johnson (Compt. Rend. lvi. p. 140) came to the conclusion that lead is all the more acted upon the purer it is, and that an energetic action only takes place above the specific gravity of 140° Tw. Similar results were obtained by Mallard (Bull. Soc. Chem. 1874, ii. p. 114) and Hasenclever.

Bauer (Berl. Ber. 1875, p. 210) found that 50 grams of strongest oil of vitriol (168° Tw.) with 0·2 gram of pure lead produced a sensible evolution of gas at 175°, stronger at 196°; at 230°-240° suddenly all the lead is changed into sulphate, with formation of SO_2, H, and S. Lead containing varying quantities of bismuth (0·71 or 4 or 10 per cent.) was even more strongly acted upon, whilst small quantities of antimony and copper make the lead more resisting; platinum acts in a similar way. Lead containing 10 per cent. tin behaves like pure lead.

According to experiments made by J. Glover (Chem. News, xlv. p. 105), pure lead is less acted upon when suspended in a vitriol chamber than such containing 0·1 to 0·75 per cent. copper, or 0·1 to 0·5 per cent. antimony. N. Cookson (ibid. p. 106) found that strong acids at a high temperature act more upon lead containing antimony than upon pure lead, whilst weaker acid at a lower temperature acts the other way. Comp. also Mactear (Chem. News, xli. p. 236).

In the North of England those rolling-mills which roll the sheet-lead from the vitriol-works supply a special kind of "chemical lead" which is made from the melted-up old chamber-lead, pipes, &c.; in this case many impurities, especially antimony, from "regulus"-valves, &c., get into the lead, which are supposed to improve its quality for acid-chambers.

Napier and Tatlock (Chem. News, xlii. p. 314) found that the action of sulphuric acid on lead at the ordinary temperature is accompanied by an evolution of hydrogen, which may cause bulging out of the closed lead vessels in which the acid is sometimes sent out for sale.

The experiments of Veley (J. Soc. Chem. Ind. 1891, p. 211), according to which mixtures of nitrous and nitric acid have a stronger action on lead than either acid by itself, have no practical bearing on the behaviour of the acid in vitriol chambers, since if nitric acid occurs there it is always accompanied by nitrous acid, and, what is far more important, the immense excess of sulphuric acid greatly modifies all conditions of the case.

An extensive investigation made by myself together with E. Schmid has been published in Zsch. f. angew. Chem. 1892, p. 642, also partly in Journ. Soc. Chem. Ind. 1891, p. 146. I here give a very brief summary of our results, some of which are of great practical importance.

1. *At higher temperatures* the *purest* lead in all cases resists both pure and nitrous sulphuric acid, with or without access of air, much better than "regulus metal" (82 Pb, 18 Sb) or "hard lead" (1·8 per cent. Sb), or even soft lead with only 0·2 per cent. Sb. *In the cold,* lead with 0·2 per cent. Sb is very slightly superior to the purest lead; regulus metal behaves much worse, and hard lead worst of all.

2. *Concentrated nitrous vitriol* is always more active than pure acid. In the case of somewhat dilute acid (spec. grav. 1·72 to 1·76), nitrous vitriol acts less than pure acid on soft lead and hard lead, owing to a protective coating of lead sulphate being formed. If more dilute, the action is again stronger (comp. below). In all cases nitrous vitriol acts more in the presence than in the absence of air.

3. Comparing two samples of soft lead, the purer sample was

found decidedly better; even a very slight proportion of bismuth (0·044 per cent.) acts injuriously.

4. It is altogether inadmissible to judge of the resistance of lead to sulphuric acid from the quantity of the *gas* (hydrogen) evolved. Soft lead gives off at the ordinary temperature, after a week's contact, much gas; hard lead, although losing much more weight, very little gas ($\frac{1}{200}$ of the theoretical quantity), probably owing to galvanic action. But, on this account, if sulphuric acid is to be sent out in tightly-closed or soldered-up leaden boxes, they should not be made of soft, but of hard lead, since otherwise the hydrogen may bulge up or burst the vessels.

5 (*a*). Lead containing up to 0·2 per cent. *copper* (alloys containing more copper cannot be homogeneously rolled) is ***in the cold*** acted upon by strong sulphuric acid more than pure lead; with nitrous acid there is not much difference. At 100° C. all kinds of acid act in the same way on pure lead and on lead containing copper; concentrated pure acid rather less than concentrated nitrous vitrol, but more than nitrous vitriol of spec. grav. 1·72 (comp. No. 2). At 200° C., concentrated acid acts alike on pure lead and on lead containing 0·02 per cent. Cu; lead containing more copper is slightly less acted upon by pure acid, but rather more by nitrous vitriol.

(*b*) Above 200° (225° to 255°) lead alloyed with 1 per cent. antimony is far more strongly acted upon than pure lead (in the proportion of 26·5 to 1 at 225°); but lead containing 0·2 per cent. copper resists the acid at 235° much *better* than pure lead in the proportion of 1 : 17, and at 255° in the proportion of 1 : 26·5.

6 (*a*). Pure soft lead gives no visible evolution of gas with pure concentrated sulphuric acid up to 220°. From this point more gas-bubbles are continually given off, and at 260° the lead is momentarily dissolved with strong frothing, smell of SO_2, and precipitation of sulphur, the temperature rising to 275°.

(*b*) The same lead, alloyed with 0·2 per cent. of copper, shows a visible evolution of gas only at 260°, regularly increasing up to the boiling-point (310°), at which the lead is very gradually dissolved.

(*c*) Soft lead, alloyed with 1 per cent. Sb, gives with sulphuric acid the first visible gas at 175°, more strongly at 225°, and between 275° and 280° there is the same turbulent, sudden solution as in the case of pure, soft lead. [Bauer, Berl. Ber. 1875, p. 210, found similar results; according to him 0·73 per cent. *bismuth* lowers the temperature of sudden decomposition from 240° to 160°.]

Hence the purest lead is subject to instantaneous solution by sulphuric acid at 260°. An addition of 1 per cent. Sb raises this temperature only about 20°, but 0·2 per cent. Cu completely destroys this liability to sudden decomposition.

7. The percentage of *oxygen* in lead is very slight even in extreme cases, and does not seem to have any connection with its liability to be acted upon by acid. But the latter, as may be imagined, is less when the *density of the surface* is *mechanically* increased.

8. The final considerations in selecting the kind of lead best suited for constructing apparatus for the manufacture of sulphuric acid are as follows :—

For vitriol-chambers, towers, tanks, pipes, and all other instances where the temperature can rise but moderately, and certainly never up to 200°C., the purest soft lead is preferable to every other description of lead, being least acted upon by hot acid, whether dilute or concentrated, pure or nitrous.

Any sensible proportion of antimony is in nearly all cases *injurious*; *copper* causes at least no improvement. This, of course, does not apply to those cases where the lead requires an addition to its tensile strength, nor to that mentioned *sub* No. 4 of packages for acid to be closed air-tight. Hence an addition of about 0·2 per cent. antimony may be useful in the case of apparatus which is only in contact with *cold* acid; but with *warm* acid even this percentage is to be avoided.

For *very high temperatures, e. g., the hottest boiling-down pans,* which ought not to be heated above 200° C., but may sometimes be raised to that point, *an addition of* 0·1 *to* 0·2 *per cent. copper is advantageous,* while antimony should be avoided here under all circumstances (comp. no. 6 *b*). That percentage of copper has no action at 200°, but only above 220°; and in the presence of bismuth it protects the lead from the sudden destruction sometimes observed.

9. Technical *"sulphuric monohydrate"* at 50° C. *acts far more strongly on lead than concentrated sulphuric acid.* [The "monohydrate" employed in our experiments had attracted a little water and tested only 98·85 per cent. H_2SO_4: its action upon lead was 13½ times that of ordinary concentrated acid of 96·5 per cent.

H_2SO_4. Fresh monohydrate of 99·5 or 99·75 per cent. would, no doubt, have shown even more action.]

10. *Nordhausen fuming oil of vitriol* acts upon lead much more strongly than ordinary concentrated acid. When it contains 20 per cent. free SO_3 it has 32 times the effect of ordinary acid; stronger Nordhausen acid has rather less effect than the 20 per cent. acid, because a protective coat of lead sulphate is formed. At all events lead must not be brought into contact with Nordhausen acid.

11. *Nitric acid* of spec. grav. 1·37 to 1·42 may be brought into contact with lead *at the ordinary temperature*, but no acid of less strength. Stronger acid than the above acts more powerfully upon lead, but no more than concentrated sulphuric acid. *Mixtures of concentrated sulphuric acid and strong nitric acid* act very little indeed upon lead, much less than either strong sulphuric acid or strong nitric acid by themselves: such mixtures can be treated in lead vessels without any hesitation. (Later observations have shown that this applies only to ordinary temperatures and when no moisture can be attracted from the air. Hot mixed acids act strongly on lead.)

12. Mixtures of *sulphuric acid and nitroso-sulphuric acid*, partly also containing *nitric acid*, all of them originally containing 0·1 per cent. N, but by heating to 65° C. brought to the state in which they can really exist in vitriol-chambers, give the following results:—If a little nitric acid is added to dilute sulphuric acid, and the mixture is heated, a little HNO_3 is volatilized, but no nitrosyl-sulphuric acid is formed until the concentration has reached spec. grav. 1·5. From this point oxygen escapes, and at spec. grav. 1·768 the whole of the HNO_3 has vanished, SO_5NH appearing in its stead. Inversely, nitric acid is formed from nitrous sulphuric acid on diluting it; in the case of prolonged heating, this evidently takes place not by splitting up into HNO_3 and NO, but by absorption of oxygen from the air.

The action of the acid on lead is least just about the lowest point where the nitrosyl-sulphuric acid is still capable of existing. It increases with its dilution, and in proportion to this, evidently through the formation of nitric acid, equally with its concentration, and later on rapidly so, the action of stronger sulphuric acid combining with that of nitrosyl-sulphuric acid and nitric acid. *The minimum action is between spec. grav.* 1·5 *and* 1·6—*that is, just at that concentration above or below which the acid ought not to be* *kept in vitriol-chambers.* This proves that it is not rational to keep the acid in the first chamber too strong (comp. Chap. VII.).

Bismuth is generally (as shown above) considered very injurious to the resisting-quality of lead for sulphuric acid. H. O. Hofmann (Min. Ind. v. p. 398) certainly states that bismuth up to 2 per cent., or up to the amount usually found in commercial lead, does not affect its resistance in vitriol-chambers, and that it is far more important that the surface should be clean and smooth, to prevent droplets of condensed acid adhering to the lead. While the second part must be accepted without contradiction, the first (concerning the bismuth) is contrary to every other experience. In a special case which has come under my notice, two Glover towers behaved quite differently, one of them going without lead repairs for 13 years, the other one being damaged before two years were over. Analysis proved the lead to be of almost identical composition in both cases; but the first contained 0·004, the second 0·012 per cent. bismuth.

According to Junge (Sächs. Jahrb. f. Berg- u. Hüttenwesen, 1895) some acid-makers prefer lead desilverized by the Pattinson process to that treated by the Parkes process, because the latter is supposed to contain more zinc; but Hofmann proves this to be contrary to facts; Parkes lead contains less zinc, but more bismuth, than Pattinson lead. It is not denied that in concentrating-pans Pattinson lead stands better than Parkes lead. This would be explained by the fact that Pattinson lead contains more copper and less bismuth than Parkes lead (comp. *supra*, p. 209).

Fluorine sometimes occurs in blende, and the fluorides may cause trouble, as they are converted into HF in the Glover tower, and this acid contaminates the sulphuric acid. Trost (Chem. Zeit. 1902, p. 12) asserts that even a very slight quantity of HF in sulphuric acid causes great wear and tear of the lead of Glover towers and chambers, not only directly, but by facilitating the corrosion by sulphuric acid and the nitrogen acids. Most descriptions of blende contain only traces of fluorine, but once he found 7 per cent. (The experiments quoted in the original do not show any essential difference between pure acids and those containing up to 2 per cent. HF in their action on lead. Gaseous HF seems to act much more than that contained in sulphuric acid.)

About the behaviour of *zinc* towards sulphuric acid, I will only quote the fact that concentrated acid yields hydrogen, together with hydrogen sulphide, down to acid of the formula SO_4H_2, 5 H_2O. Acid of the formula SO_4H_2, 6 H_2O yields pure hydrogen (Muir and Robb, Chem. News, xlv. p. 70).

Tin is not acted upon by acid of the formula SO_4H_2, 3 H_2O.

Behaviour of Sulphurous and Sulphuric Acid towards the Oxides of Nitrogen.—The reactions between the oxides and acids of sulphur and nitrogen are of extreme importance for the theory of the sulphuric acid process in general, and for the recovery of the nitrogen compounds in particular.

The older researches in this field, of Clément-Desormes, Dalton, Davy, Berzelius, Gay-Lussac, W. Henry, Gaultier de Claubry, De la Provostaye, A. Rose, Koene, Weltzien, Rebling, and Müller, have now merely an historical interest. The modern literature of this subject begins with the labours of R. Weber, during the years 1862 to 1867, published in the Journ. f. prakt. Chem. lxxxv. p. 423 and c. p. 37; Poggendorff's Annalen, cxxiii. p. 341, cxxvii. p. 543, cxxx. p. 277; and partly in Dingler's Polyt. Journal, clxvii. p. 453. Other very important papers have been published by Cl. A. Winkler ('Researches on the Chemical Processes going on in the Gay-Lussac Towers,' Freiberg, 1867), by Rammelsberg (Ber. d. deutsch. chem. Gesellsch. 1872, p. 310), by Michaelis and Schumann (ib. 1874, p. 1075).

My own researches referring to this subject are found in the following publications:—1877: Berl. Ber. x. pp. 1073 & 1432. 1878: Berl. Ber. xi. pp. 434 & 1229; Dingler's Journal, ccxxviii. pp. 70, 548, & 553. 1879: Dingler's Journal, ccxxxiii. p. 63; Berl. Ber. xii. pp. 357 & 1058. 1881: Berl. Ber. xiv. pp. 2188 & 2196. 1882: Berl. Ber. xv. pp. 488 & 495. 1884: Chem. Ind. 1884, p. 5. 1885: J. Soc. Chem. Ind. pp. 31 & 447; Berl. Ber. xviii. pp. 1376, 1384, 1391; J. Chem. Soc. xlvii. pp. 457 & 465. 1888: Berl. Ber. xxi. pp. 67 & 3223. 1889: Zeitsch. f. angew. Chemie, pp. 265 & 385. 1890: ibid. p. 195. 1899: ibid. p. 393.

Of the different oxides of nitrogen, *nitrous oxide*, N_2O, need not detain us here. It is very slightly soluble in sulphuric acid, much less so than in pure water, as, once formed, it is not oxidized again into NO or higher nitrogen oxides; it is altogether lost for the manufacture of sulphuric acid, nor does it form any chemical compound with that acid.

Nitric oxide, NO, was said by Henry and Plisson to be absorbed by oil of vitriol, if left a long time in contact with it, with formation of nitrous pyrosulphuric anhydride (see below); but Berzelius, Gay-Lussac, and many others have long ago refuted this statement, more especially Winkler (*l. c.* p. 58). In fact the sulphuric acid of the absorbing-apparatus cannot retain that portion of the nitrogen oxides which have been reduced to the state of nitric oxide; and from this follows the necessity of an excess of oxygen in the gas issuing from the chambers, since only this prevents the existence of nitric oxide in the same. Small quantities of nitric oxide may, however, escape oxidation even in the presence of oxygen, and are hence found in the chamber exit-gases.

The solubility of NO in sulphuric acid, although not *nil*, is extremely slight. Cl. Winkler already in 1867 showed that it is not absorbed by strong vitriol. Kolb also made experiments with acids of varying concentration (Bull. Soc. Indust. Muhl. 1872, p. 225), and has found that acid of 1·841 does not absorb even traces of NO; acid of 1·749 to 1·621 merely traces (2 to 6 milligrams to 100 grms. acid); acid of 1·426 absorbs 0·017 grm. NO; acid of 1·327, 0·020 grm. NO to 100 grms. My own experiments (Journ. Soc. Chem. Ind. 1885, p. 447, and 1886, p. 82; also Berl. Ber. 1885, p. 1391, and 1886, p. 111) show that concentrated O.V. absorbs per c. c. only 0·0000593 grm. = 0·035 c. c. NO, and acid of sp. grav. 1·500 only half that quantity.

In the presence of oxygen nitric oxide is absorbed by sulphuric acid (Bussy, Winkler); but then it is really nitrous acid which is absorbed; and Winkler was the first to prove that it is precisely the presence of sulphuric acid which causes the oxidation not to proceed beyond the formation of nitrous acid, the latter combining afterwards with the sulphuric acid to form nitroso-sulphuric acid and water:—

$$2\,SO_2(OH)_2 + N_2O_3 = 2\,SO_2(OH)(ONO) + H_2O.$$

In several of the above-quoted papers I have given clear proofs of the same fact, viz., that on passing nitric oxide, together with a very large excess of free oxygen, through strong sulphuric acid, nothing but nitroso-sulphuric acid is formed, which means that 2NO take up only 1 O; but once out of the range of the acid, immediately above it, the reaction $2\,NO + O_2 = N_2O_4$ sets in, and this compound, when afterwards meeting sulphuric acid, yields equal molecules of nitric acid and of nitroso-sulphuric acid (*vide infrà*).

Nitrous acid.—Real nitrous acid, HNO_2, is not known in the pure state, only in that of dilute solutions. When dissolving nitrous anhydride, N_2O_3, in water, some nitrous acid is formed and remains dissolved in the excess of water, but much splits up according to the formula:

$$3\,NO_2H = 2\,NO + NO_3H + H_2O.$$

The anhydride, N_2O_3, also called nitrogen tetroxide, is known as a dark blue liquid which boils below 0° C. The vapours immediately dissociate for the most part into NO and NO_2 (with more or less N_2O_4, according to temperature), but a small quantity of N_2O_3 evidently exists even in the state of vapour. We shall not here enter upon the much debated question concerning the existence of N_2O_3 in the gaseous state, but merely quote the literature: Luck (Berl. Ber. 1878, pp. 1232 & 1643), Witt (ibid. p. 2188), Ramsay & Cundall (Journ. Chem. Soc. xlvii. pp. 187, 672), Lunge (ibid. p. 457; Zsch. anorg. Chem. vii. p. 209), and Dixon & Peterkin (Proc. Chem. Soc., May 1899, p. 115).

Although there is no doubt about the fact that most of the "nitrous vapours," formerly considered as N_2O_3 in the state of gas or vapour, is in reality principally a mixture of nitrogen oxide (NO) and peroxide (which, for the sake of simplicity, we shall in this case consider as NO_2), with very little N_2O_3, we must bear in mind the equally undoubted fact that a mixture of equal molecules of NO and NO_2 behaves in all its reactions towards other chemical compounds exactly as if it were N_2O_3. When passed into an alkaline solution, it quantitatively yields a nitrite :

$$2\,NaOH + NO + NO_2 = 2\,NaNO_2 + H_2O.$$

When brought into contact with concentrated sulphuric acid it is quantitatively converted into nitroso-sulphuric acid :

$$2\,H_2SO_4 + NO + NO_2 = 2\,SO_5NH + H_2O.$$

We have, therefore, the right to assume that such a mixture of equal molecules of NO and NO_2 *chemically* comes to the same thing as gaseous N_2O_3; and we shall throughout this book simplify many of our explanations and discussions by speaking of the above mixture as N_2O_3, although *physically* it is only a mixture of NO and NO_2. We are all the more entitled to do this, since there is no doubt that *some* N_2O_3 exists in the gaseous state as such, and since, according to the law of mass action, this N_2O_3 must be constantly reformed when taken away by some chemical reaction.

I have all the more right to take this line, since everybody speaks of distilling sulphuric acid or subliming ammonium chloride, although we know that on distillation nearly all sulphuric acid is split up into SO_3 and H_2O, which recombine on condensation (comp. p. 172), and ammonium chloride in the state of vapour is mostly $= NH_3 + HCl$.

Nitrous anhydride (*nitrogen trioxide*), N_2O_3, dissolves in sulphuric acid, all the more easily when the latter is concentrated, but also, as we shall see, when it contains a certain amount of water. The reaction taking place is this:

$$2\,H_2SO_4 + N_2O_3 = 2\,SO_5NH + H_2O.$$

Rammelsberg (*l. c.*) asserts that when nitrous anhydride is employed in excess, nitric acid and nitric oxide are also formed:

$$H_2SO_4 + 2\,N_2O_3 = SO_5NH + HNO_3 + 2\,NO\,;$$

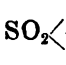
but this reaction only takes place in presence of water, and the formation of nitric acid and nitric oxide must be regarded as a secondary reaction, owing to the well-known action of free nitrous acid on an excess of water. Where there is enough sulphuric acid and no excess of water, Rammelsberg's reaction does not come into play.

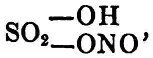
The compound formed by the action of nitrous acid on sulphuric acid of the empirical formula SO_5NH has long been known, both in the solid state, as "chamber-crystals," and dissolved in an excess of sulphuric acid, as "nitrous vitriol"; but its true composition and nature have only comparatively recently been elucidated.

The easiest way of preparing the *chamber-crystals* in a state of purity is by conducting sulphur dioxide into well-cooled fuming nitric acid until the whole mass has been converted into a magma, but not until the nitric acid has been entirely decomposed, and drying the crystallized mass on a porous slab under a bell-jar over some oil of vitriol. Obtained in this way, or collected in the connecting-pipes of vitriol-chambers or other places where there is a deficiency of steam, they consist of four-sided prisms or orthorhombic crystals; but generally, when prepared on the small scale, they appear as a scaly, feather-like, or granular mass, colourless and transparent. Their fusing-point is stated by Weltzien=73°, by Gaultier de Claubry=120° to 130°; but they are partly decomposed before fusing, with evolution of red fumes.

The composition of chamber-crystals was formerly uncertain; the question was, in the language of the older chemists, whether they were a compound of sulphuric acid with nitrogen peroxide or with nitrous acid (nitrogen trioxide). Müller (Ann. Chem. Pharm. cxxii. p. 1) still pronounced for the former; but R. Weber proved in 1862, and more rigorously in the following year, by estimating all their constituents according to unexceptionable methods, that their formula must be constructed on the second supposition. His results were as follows:—

	Molecular weight.	Calculated.	Found.
$2\ SO_3$	160	62·39	64·00
N_2O_3	76	29·92	27·96
H_2O	18	7·69	10·50
SO_3, N_2O_3, H_2O	254	100·00	102·46

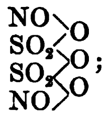
This formula has also been confirmed by Michaelis and Schumann (Ber. 1874, p. 1075), who at the same time maintained, from the products of decomposition by phosphorus perchloride, that the compound whose molecular weight has to be halved must be regarded as *nitrosulphonic acid,*  $SO_2\langle{}^{OH}_{NO_2}$—that is, as sulphuric acid, one of whose hydroxyls is replaced by the nitro group, or as nitric acid, for whose hydroxyl is substituted the sulpho group. This mode of explaining the constitution of that substance cannot, however, be strictly maintained. Both from its formation and the decomposition, it is certain that it does not contain the nitro group NO_2, but the nitroso group NO. Its formula must therefore be written:



$$SO_2{}^{-OH}_{-ONO},\ \text{or}\ SO_2(OH)(ONO),$$

and it must be called nitrosyl sulphate, or, more correctly, nitrososulphuric acid, which means sulphuric acid, one of whose hydrogen atoms is replaced by the nitroso group, that is the radical of nitrous acid, NO(OH). It is a mixed anhydride of sulphuric and nitrous acid, as is proved both by its formation and its decomposition by water.

There exists also a complete anhydride of nitroso-sulphuric acid, of the empirical formula, N_2O_3, $2\,SO_3$, which is rationally written:



but this is only formed by mixing liquid sulphur dioxide and nitrogen tetroxide in the cold under pressure (Provostaye), or sulphuric anhydride with dry nitric axide (H. Rose), or by heating sulphuric anhydride with nitrogen tetroxide (Weber), none of which reactions are possible in the manufacture of sulphuric acid.

Neither is this the case with the compound produced by R. Weber (Poggend. Annalen, clxii. p. 602) by conducting sulphuric anhydride into the most highly concentrated nitric acid, which has the empirical formula N_2O_5, $4\,SO_3$, $3\,H_2O$.

Nitroso-sulphuric acid is formed not merely as above indicated, but in many other ways. We have already mentioned its formation from sulphur dioxide and nitric acid:

$$SO_2 + NO_3H = SO_2(OH)(ONO).$$

It is also formed when a mixture of strong sulphuric and nitric acids is heated, oxygen being evolved (A. Rose):

$$H_2SO_4 + HNO_3 = SO_2(OH)(ONO) + H_2O + O.$$

On the other hand, sulphur dioxide can form that compound even with the lower oxides of nitrogen, if there is water and (except with N_2O_4, where this is unnecessary) oxygen present. In the perfectly dry state sulphur dioxide does not act on the dry nitrogen oxides; but in presence of the smallest quantity of water "chamber-crystals" are formed, if SO_2 meets with N_2O_4, or with NO or N_2O_3 and oxygen. Winkler has shown that, in an atmosphere of moist carbon dioxide, nitrogen trioxide does not form chamber-crystals with sulphur dioxide, but nitrogen peroxide does so, and he distinguishes N_2O_3 and N_2O_4 in this manner. The fumes of N_2O_3, with an excess of SO_2 and H_2O, but in the absence of oxygen, give no chamber-crystals at all; they are decolorized, nitric oxide and sulphuric acid being formed. If oxygen or air is admitted, chamber-crystals instantly appear, and this is also the case when nitrogen peroxide meets sulphurous acid in the presence of water. These observations of Winkler's have been repeatedly confirmed; but we must now add that what he called "fumes of N_2O_3" is in reality mostly a mixture of equal molecules of NO and NO_2, behaving *chemically* like N_2O_3.

As some points had not been entirely cleared up by previous investigators, and there were partial contradictions among their results, I undertook a new investigation on the ***interaction of sulphur dioxide and nitric oxide, with or without the presence of water*** (Berl. Ber. xiv. p. 2196), which led to the following results:—

1. Dry NO and SO_2 have no action upon one another, be it at the ordinary temperature, or at 50° or at 100°, provided that air and moisture are rigorously excluded.

2. NO, SO_2, and water act in such a way that as much N_2O is formed as corresponds to the quantity of SO_2 originally present. A reduction down to N could not be established.

3. If NO and SO_2 meet in the presence of dilute sulphuric acid, of spec. grav. 1·455, no reduction of NO to N_2O takes place, even when there is a very large excess of SO_2 present, whether the digestion be carried on for many hours at ordinary temperature or at 60°. Even with acid of spec. grav. 1·32 no reduction of NO by SO_2 could be established.

4. If NO, SO_2, and oxygen meet in the presence of water, a slight but distinct reduction down to N_2O takes place. If, however, in lieu of water, dilute acid of spec. grav. 1·32 is employed, no such reduction can be observed.

The bearing of these results on the theory of the chamber-process will be discussed later on (Chapter VII.).

A further investigation by myself (Berl. Ber. xviii. p. 1384; Journ. Chem. Soc. xlvii. p. 465) confirmed the above results. It was shown that in the dry state nitric oxide combines with an excess of oxygen to form N_2O_4 exclusively, or nearly so; dry nitric oxide in excess with oxygen yields N_2O_3 along with N_2O_4; in the presence of water, NO with an excess of oxygen is altogether converted into nitric acid. If, however, NO meets O in immediate contact with concentrated sulphuric acid, there is neither N_2O_4 nor HNO_3 formed, even with the greatest excess of oxygen; oxidation proceeds only to the stage of N_2O_3, which, however, is not formed in the free state, but passes into nitrososulphuric acid :

$$2\,SO_4H_2+2\,NO+O=2\,SO_2(OH)(ONO)+H_2O.$$

Outside the immediate contact with the acid the reaction is again as before with dry gases, viz. $2\,NO+O_2=N_2O_4$; that is, here NO is oxidized to a higher state than within the sulphuric acid.

A very elaborate investigation of the interaction between nitrous and sulphurous acid was published by Raschig (Lieb. Ann. ccxli. pp. 161 *et seq.*). He found a number of new compounds, and rectified some of the statements of Frémy and Claus concerning compounds formerly described by them. He also discovered a very convenient method of preparing hydroxylamine. But as nearly all Raschig's experiments were made with alkaline solutions, and those which were performed with acid solutions were made under conditions utterly different from those of a lead chamber, namely at the freezing-point, we cannot stop to give any details of his results. Under the just-mentioned circumstances, apart from N_2O and NO, amidosulphonic acid, hydroxylamine, and ammonia are observed, but only in small quantities; and above the low temperatures employed by Raschig the occurrence of those substances is altogether too uncertain and minimal to be taken into consideration for our purposes.

Action of water on chamber-crystals.—These crystals are very deliquescent; they absorb water rapidly from ordinary air. In contact with a little more water, they dissolve quickly with evolution of heat, much nitric oxide being given off. When introduced into a large quantity of water, they dissolve without visible evolution of gas ; but in point of fact nitric oxide is formed as well, also nitric acid, together with nitrous acid. This has led to many attempts at explanations, and Rammelsberg and Philipp have asserted that exactly $\frac{1}{4}$ of the nitrogen appears as NO, $\frac{5}{8}$ as nitrous acid, and $\frac{1}{8}$ as nitric acid :

$$16\,SO_2(OH)(ONO)+9H_2O=16\,SO_4H_2+4NO$$
$$+2NO_2(OH)+5N_2O_3.$$

But this complicated and very unlikely reaction need not be assumed at all. Every fact observed in this connection can be quite simply explained by the following reaction:

$$SO_2(OH)(ONO) + H_2O = SO_4H_2 + NO(OH) ;$$

that is, nitroso-sulpuric acid takes up the elements of water, to form sulphuric acid and nitrous acid; the latter, as is well known, is unstable in the presence of an excess of water, and hence partly splits up into nitric oxide and nitric acid:

$$3\,NO_2H = NO_3H + 2\,NO + H_2O.$$

In the presence of less water, nitrous anhydride can be formed from chamber-crystals, and escapes in the shape of brown fumes (of course mostly dissociated into nitric oxide and peroxide):

$$2\,SO_2(OH)(ONO) + H_2O = 2\,SO_4H_2 + N_2O_3.$$

For nearly every purpose nitroso-sulphuric acid or its solution in sulphuric acid may be regarded as a solution of nitrous acid in sulphuric acid.

The behaviour of nitroso-sulphuric acid towards sulphuric acid of various concentrations is of great interest for our purposes. In concentrated oil of vitriol the crystals dissolve easily and without decomposition. This solution is stable enough to be distilled without losing any nitrous acid, whilst the isolated crystals are decomposed on being gently heated. I have shown (Zeitsch. f. angew. Chemie, 1888, p. 661, and 1890, p. 447) that on distilling such a solution for four hours, when 40 per cent. of the sulphuric acid had passed over, the distillate contained only 5 per cent., the residue 95 per cent. of the nitrous acid, none of it having been destroyed. It is possible to obtain solutions of 1·9 sp. gr.; they evolve with water nitric oxide, inflame phosphorus at 62° C., oxidize sulphur and many metals on distillation with evolution of NO; heated with ammonium sulphate to 160° they evolve nitrogen gas. Sulphur dioxide evolves nitric oxide; but a solution of nitroso-sulphuric acid in strong oil of vitriol (of 170° Tw.), even on long-continued treatment with dry sulphur dioxide, is only incompletely decomposed, and on addition of water still shows the presence of nitrous acid by the evolution of brown vapours. This explains the fact (well known to manufacturers) that *concentrated* sulphuric acid contaminated by nitrous acid is only with difficulty purified by sulphur dioxide. At a higher temperature sulphur dioxide decomposes chamber-crystals with evolution of nitrous oxide (Frémy). Further statements respecting the behaviour of sulphur dioxide towards the solution of chamber-crystals in sulphuric acid, the so-called "nitrous vitriol," will be made when examining the process going on within the Glover tower. It is remarkable, and of great importance for the practice of sulphuric-acid making, that even dilute acids of 1·70 down to 1·55 sp. gr. dissolve the crystals in the cold without decomposition; the decomposition only commences when the specific gravity of the dilute acid has fallen below 1·55—that is, below the density of ordinary chamber-acid.

Nitrogen peroxide[*], whether in the state of a liquid or a gas, strongly acts on sulphuric acid. If, according to Weber, nitrogen peroxide, made by gently heating fuming nitric acid [and therefore not quite free from nitric acid], be added to sulphuric acid of different degrees of concentration, the following is observed:—The strongest oil of vitriol, down to 1·7 sp. gr., absorbs the nitrogen peroxide without coloration. Acid of 1·55 turns yellow; here the nitrogen peroxide is probably absorbed to a large extent similarly as by nitric acid, and no decomposition, as represented by the equation on page 223, has taken place, whilst this has to be assumed in the case of the stronger acids. Acid of 1·49 turns greenish yellow; of 1·41 intensely green; acid of 1·31 turns blue and evolves nitric oxide, which on applying a gentle heat escapes with violent effervescence. Weak acids are only coloured for a short time. From this Weber inferred:—that acids of 1·8 to 1·7 combine with nitrogen peroxide with formation of nitroso-sulphuric acid; weaker acids simply absorb it; and the more dilute acids decompose it with formation of nitric oxide, nitrous acid, and nitric acid. The action of sulphurous acid on these mixtures is different according to their concentration. As mentioned above, the solution of chamber-crystals in concentrated sulphuric acid is but incompletely decomposed even by a prolonged action of sulphurous

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[*] We shall generally give this name to the compound formerly called "hyponitric acid" and now sometimes "nitrogen tetroxide" or "nitrogen dioxide." It is well known that in the gaseous state it consists of a mixture of molecules of NO_2 and N_2O_4, of varying proportions, according to the temperature. At a low temperature, especially in the liquid state, it is $=N_2O_4$; above $140^{\circ} = NO_2$. The following are the intermediate proportions:—

At 26·7 °C.	80	per cent. N_2O_4,	20	per cent. NO_2.
„ 39·8 „	71	„ „	29	„ „
„ 60·2 „	47	„ „	53	„ „
„ 80·6 „	23	„ „	77	„ „
„ 135 „	1	„ „	99	„ „

acid; but the yellow mixture of 1·55 sp. gr. and the coloured, more dilute, acids are decomposed with strong effervescence of nitric oxide. It will be shown afterwards what part all these reactions play in the recovery of the nitrous gas in the manufacture, where the object is first to absorb the gas in sulphuric acid of 1·7, and then again to liberate it from that solution.

Winkler gave a different account of the behaviour of liquid nitrogen peroxide from that of Weber. He stated that it may be mixed with sulphuric acids down to 142° Tw., but that it yields a solution totally different from that of chamber-crystals in sulphuric acid, viz., one of a yellow colour and constantly evolving red fumes. On heating, it effervesces and gives off streams of gaseous nitrogen peroxide; if the mixture is made with sulphuric acid of 142° Tw., the NO_2 completely volatilizes far below the boiling-point of sulphuric acid, so that the residue on dilution with water does not decolorize potassium permanganate. If, however, acid of 170° Tw. has been employed, the liquid on heating certainly yields up the larger portion of its NO_2; but the residue behaves like a solution of chamber-crystals in sulphuric acid, and on being mixed with water it evolves red fumes which can be proved to be N_2O_3, not NO_2, by their not forming any chamber-crystals with moist SO_2.

There are some essential differences between the statements of Weber and those of Winkler, more especially so far as the behaviour of nitrogen peroxide is concerned, which were cleared up by my own researches (see below).

If concentrated sulphuric acid is mixed with a little concentrated *nitric acid*, and sulphur dioxide is passed into the mixture, the nitric acid in the cold is only reduced to nitrous acid, which remains combined with the sulphuric acid: this compound resists the further action of the sulphur dioxide, similar to the solution prepared from concentrated oil of vitriol and chamber-crystals. On the other hand, more dilute mixtures of sulphuric and nitric acid, below 1·7 spec. grav., are more or less easily decomposed by SO_2, in the ratio of their dilution.

Since the labours of Weber and Winkler did not in all points agree with one another, and the subject seemed to call for another investigation, I undertook a long research (Dingler's Journal, ccxxxiii. p. 63), the conclusions of which (also published in the Berl. Ber. xii. p. 1058) are as follows:—

1. Nitrogen peroxide, under ordinary circumstances, cannot exist in contact with sulphuric acid, but at once splits up into nitrous acid, which, with a portion of the sulphuric acid, yields nitroso-sulphuric acid and nitric acid (dissolving as such), thus :—

$$N_2O_4+SO_2(OH)_2=SO_2(OH)(ONO)+NO_3H.$$

2. Nitroso-sulphuric acid, on dissolving in an excess of sulphuric acid, forms a colourless liquid, but only up to a certain limit of saturation, which is all the higher the more concentrated the sulphuric acid. This limit for acid of sp. gr. 1·84 is not yet reached at 55·34 milligrams $N_2O_3=185$ millig. $SO_2(OH)(ONO)$ in 1 cubic centim. of acid.

3. Beyond that limit at first a yellowish tint appears, of course with stronger acids only when more nitroso-sulphuric acid is present than with weaker acids. This took place with a mixture of sp. gr. 1·887 (made from pure sulphuric acid of sp. gr. 1·84), containing in 1 cub. centim. 147 milligrams $N_2O_3=372$ milligr. $SO_2(OH)(ONO)$, and also with acid of sp. gr. 1·706, containing in 1 cub. centim. only 56·7 milligr. $N_2O_3=190$ milligr. $SO_2(OH)(ONO)$. Since these acids also are rendered colourless by prolonged boiling, the excess of nitroso-sulphuric acid seems to be rather loosely held; but the temperature of the water-bath is not sufficient to affect it.

4. The phenomenon observed by Winkler, a mixture of strong vitriol and nitrogen peroxide showing an orange-colour even when cold, emitting red vapours, and exhibiting a tempestuous evolution of nitrogen peroxide on being gently heated (which proves the existence of unchanged nitrogen peroxide), can evidently take place only when the mixture contains *far* more N_2O_4 than the strongest mentioned above, or the strongest ever occurring in vitriol-works under any circumstances. Many experiments of heating in the water-bath for a prolonged period demonstrate the absence of free N_2O_4 in all cases observed. Still less can the presence of nitrogen peroxide be assumed in more dilute acids; it is therefore inadmissible to cite it as such in analyses.

5. All nitrous vitriols, *i. e.* solutions of nitroso-sulphuric acid in sulphuric acid, whether they contain nitric acid at the same time or not, on being heated far below their boiling-point assume a golden-yellow or even darker yellow colour, but entirely lose it again on cooling. This change of colours may be repeated any

number of times. It hardly indicates a loosening of the combination, since this proves to be very stable even at much higher temperatures; but it may rather be compared to the deeper colour which ferric-chloride solutions assume on being heated.

6. The stability of nitroso-sulphuric acid in its solution in sulphuric acid is very great, even at the boiling-point, providing the specific gravity is not below 1·70. It is true that on boiling it some nitrogen is always lost, and all the more the less concentrated the acid is; but if the boiling takes place so that the vapour cannot condense and flow back, there is some nitroso-sulphuric acid found in the residue, even from acid of sp. gr. 1·65 (comp. p. 221). But if the vapour is condensed and the condensing liquid (which, in the case of vitriol of sp. gr. 1·80 or below, consists of very dilute acid or almost pure water) is allowed to flow back, a considerable loss is caused by denitration.

7. Down to a concentration of sp. gr. 1·65 the affinity of sulphuric acid for nitrous acid, *i. e.* the tendency to the formation of nitroso-sulphuric acid, is so great that any nitric acid present at the same time, whether added as such or formed by the decomposition of nitrogen peroxide, is reduced with loss of oxygen, and employed to form nitroso-sulphuric acid. In the case of acid of sp. gr. 1·71 and upwards, this transformation takes place almost completely after a brief boiling, but at sp. gr. 1·65 only incompletely. This is a further argument against the existence of N_2O_4 in the solution.

8. Below sp. gr. 1·65 the nitroso-sulphuric acid possesses so little stability that, for instance, from acid of sp. gr. 1·60 some nitrogen oxides (but only a very small percentage) are expelled in the water-bath, and nearly all of them by boiling for a short time. In the case of acid of sp. gr. 1·5, it is evident that, even without heating, the nitrous acid added is partly decomposed into nitric acid and nitric oxide; but after heating for an hour in the water-bath a considerable quantity of nitroso-sulphuric acid remains undecomposed, whilst another portion has been converted into sulphuric acid. In the case of still weaker acids, of course these phenomena occur even to a greater extent; but it is very probable that even very dilute sulphuric acid may contain, while cold, a little nitroso-sulphuric acid if reducing-agents are absent.

9. Most of the nitric acid present along with nitroso-sulphuric acid in dilute acids (of sp. gr. 1·5 and under) remains behind in

the liquid even after prolonged boiling. If, therefore, the nitrous vitriol of acid-works, in consequence of a faulty process, contains nitric along with nitrous acid, it cannot possibly be completely denitrated by hot water or steam, in which case a less strength than sp. gr. 1·5 is never reached; the denitration can be only effected by reducing-agents, such as sulphur dioxide in the Glover tower or mercury in the nitrometer. In the latter it can be very clearly seen with how much more difficulty and slowness the denitration goes on in the presence of nitric acid.

10. The tendency to form nitroso-sulphuric acid is so strong that even if a large quantity of air (oxygen) is passed through sulphuric acid along with nitrous acid no oxidation to N_2O_4 or N_2O_5 takes place, just as in the case of oxygen and NO.

11. Nitrous acid cannot be absorbed by caustic-soda solution without loss, because a portion of it is decomposed into nitric acid and nitric oxide.

12. The purple colour which is developed in nitrous vitriol by the action of reducing-agents is caused by a solution of nitric oxide in such acids, and is possibly produced by a very unstable compound of nitrogen and oxygen, midway between NO and N_2O_3.

Although my experiments had decidedly proved (comp. No. 1 and 4 of the just-quoted conclusions) that nitrogen peroxide does not dissolve as such in sulphuric acid, with formation of an unstable solution from which the N_2O_4 can be drawn off by heating, the former erroneous assertion of Winkler (since that time recognized as such by himself) did not vanish from chemical literature, and, for instance, gave rise to a decidedly erroneous explanation of the process of Lasne and Benker for treating the absorption in the Gay-Lussac tower. This caused me to investigate the subject once more (Berl. Ber. xv. p. 488). I pointed out that mixtures of pure nitrogen peroxide with even somewhat dilute sulphuric acid, down to spec. grav. 1·65, behave quantitatively as mixed solutions of equal molecules of nitroso-sulphuric acid and nitric acids; that on prolonged heating in a water-bath such solutions in acid of spec. grav. 1·75 do not lose any, and in acid of spec. grav. 1·65 only very little, of their nitrogen compounds. On prolonged boiling part of the latter escapes, but a large quantity of nitroso-sulphuric acid remains behind, more than that originally present, part of the nitric acid having passed into it with loss of oxygen. The idea of a "loose" union between N_2O_4 and sulphuric acid must therefore be entirely abandoned; and from this follows the fallacy of the idea held by some manufacturers that N_2O_4 is less easily absorbed by sulphuric acid than N_2O_3, and that therefore much N_2O_4 is lost in the Gay-Lussac tower. I directly disproved this idea by showing that vapours of nitrogen peroxide are most easily, quickly, and completely absorbed by sulphuric acid of spec. grav. 1·71, such as is used in the Gay-Lussac tower, and that this (colourless) solution is not changed either by long heating to 100° or by passing a current of air for a long time through it.

A concluding investigation on the behaviour of nitrogen peroxide towards sulphuric acid has been made by myself together with Weintraub (Zsch. angew. Ch. 1899, p. 393), of which I here give merely a summary of the results.

1. The reaction between sulphuric acid and nitrogen peroxide is reversible, since the nitric acid formed has some action on nitroso-sulphuric acid, forming sulphuric acid and nitrogen peroxide:

$$H_2SO_4 + N_2O_4 \rightleftarrows SO_5NH + HNO_3.$$

In mixtures of sulphuric acid and nitrogen peroxide an equilibrium is formed, all four substances—sulphuric acid, nitrogen peroxide, nitroso-sulphuric acid, and nitric acid—being present at the same time. 2. In contact with concentrated sulphuric acid (95 per cent. H_2SO_4) nearly all the nitrogen peroxide is converted into nitroso-sulphuric and nitric acid. The inverse reaction sets in to a sensible extent only when very little sulphuric acid is present in comparison with nitric acid. 3. The affinity of sulphuric acid for nitrogen peroxide quickly decreases with the increase of water, so that in the case of sulphuric acid of spec. grav. 1·65 the action of nitric acid on nitroso-sulphuric acid begins to prevail; therefore very much of the nitrogen peroxide added remains in the free state, although the quantity of HNO_3, which is only formed by the reaction itself, is but small. 4. In the practice of sulphuric-acid manufacture, the quantity of sulphuric acid in the concentrated state so largely prevails over that of the nitric acid, that all nitrogen peroxide may be practically regarded as quantitatively changed into SO_5NH and HNO_3. This, of course, also holds good when absorbing nitrous gases in concentrated sulphuric acid for analytical purposes. Therefore the conclusions No. 1

and No. 4 (p. 223), although not mathematically exact, are to all intents and purposes valid.

The tension of nitrous acid in presence of dilute sulphuric acid at different temperatures is a matter of great importance for the theory of the formation of sulphuric acid in the lead-chambers. The first observations on this point were published by Sorel (Zsch. angew. Ch. 1889, p. 272); but these have become obsolete by the far more extended observations published by myself in the Zeitsch. f. angew. Chemie, 1891, pp. 37 *et seq.* The tables constructed from these indicate the loss of N_2O_3 suffered by acids of four different concentrations, containing quantities of N_2O_3 varying from 1 gram per litre upwards, in a current of air at temperatures from 50° to 90° C. (pp. 228–231).

The behaviour of nitroso-sulphuric acid towards reducing reagents is of the greatest importance, both for the chamber-process in general and for the recovery of nitrogen compounds. The most important of the reagents in question is sulphur dioxide, which acts as follows:—

$$2\,SO_2(OH)(ONO) + SO_2 + 2\,H_2O = 3\,SO_4H_2 + 2\,NO;$$

that is, it forms with nitroso-sulphuric acid both sulphuric acid and nitric oxide. This is the leading reaction of the Glover tower, as we shall see hereafter; and it must also occur within the chambers, more especially in the first part of the set.

Sorel (Zeitsch. f. angew. Ch. 1888, p. 273) has shown that if a mixture of SO_2 and O is made to react upon nitrous sulphuric acid and NO, there may be either a reduction of nitrous acid to NO, or an oxidation of NO to N_2O_3 (in the shape of SO_5NH), according to variations in the following conditions: temperature, dilution of the acid, proportion between SO_2 and O, percentage of NO. The extreme cases were well known before: a reduction takes place at high temperatures, with scarcity of oxygen and excess of water; an oxidation with excess of oxygen, concentrated acid, and low temperatures. For the intermediate cases Sorel made some special experiments, from which it followed that in identical mixtures an increase of the temperature from 70° C. to 80° C. was sufficient to change the oxidation into reduction. At equal temperatures a reduction took place when the gaseous mixture contained 31 per cent. SO_2, 10 per cent. O, 59 per cent. N, but an oxidation with a mixture of 21 SO_2, 12·1 O, 66·9 N, &c. The

1. Nitrous vitriol of spec. grav. 1·720 (say, 78 per cent. H_2SO_4).

N_2O_3 originally present. Grams in 1 litre.	Loss of N_2O_3 in grams per litre at				
	50°.	60°.	70°.	80°.	90°.
1	...	...	...	...	0·006
2	...	...	...	...	0·018
3	...	...	...	...	0·025
4	...	...	...	...	0·031
5	...	...	...	...	0·037
6	...	...	...	...	0·043
7	...	...	...	0·006	0·056
8	...	...	...	0·010	0·068
9	...	...	...	0·012	0·081
10	...	...	...	0·018	0·093
11	...	...	...	0·025	0·112
12	...	...	...	0·030	0·125
13	...	...	...	0·031	0·143
14	...	...	...	0·043	0·168
15	...	...	0·006	0·056	0·193
16	...	...	0·010	0·068	0·218
17	...	...	0·006	0·087	0·250
18	...	...	0·012	0·106	0·281
19	...	..	0·025	0·125	0·318
20	...	...	0·031	0·150	0·356
21	...	...	0·043	0·175	0·400
22	...	...	0·064	0·200	0·450
23	...	0·006	0·081	0·237	0·500
24	0·006	0·018	0·100	0·275	0·550
25	0·012	0·031	0·125	0·312	0·600
26	0·018	0·043	0·150	0·356	0·662
27	0·031	0·062	0·181	0·400	0·725
28	0·043	0·081	0·212	0·450	0·800
29	0·062	0·100	0·256	0·500	0·850
30	0·081	0·125	0·293	0·550	0·956
31	0·093	0·162	0·337	0·612	1·043
32	0·112	0·200	0·387	0·641	1·125
33	0·125	0·237	0·391	0·743	1·206
34	0·143	0·275	0·475	0·806	1·287
35	0·156	0·312	0·525	0·868	1·375
36	0·175	0·350	0·575	0·931	1·456
37	0·193	0·381	0·618	1·000	1·543
38	0·206	0·418	0·662	1·062	1·625
39	0·237	0·456	0·718	1·125	1·712
40	0·268	0·500	0·775	1·193	1·800
41	0·293	0·543	0·831	1·256	1·890
42	0·325	0·587	0·887	1·331	1·975
43	0·350	0·631	0·937	1·400	2·062
44	0·376	0·675	0·993	1·468	2·150
45	0·406	0·712	1·050	1·537	2·237
46	0·437	0·756	1·106	1·606	2·325
47	0·462	0·800	1·162	1·675	2·392
48	0·493	0·837	1·218	1·743	2·500
49	0·518	0·881	1·268	1·806	2·587
50	0·550	0·931	1·325	1·875	2·675

2. Acid of spec. grav. 1·686 (say, 76 per cent. H_2SO_4).

N_2O_3 originally present. Grams in 1 litre.	Loss of N_2O_3 in grams per litre at				
	50°.	60°.	70°.	80°.	90°.
8	...	...	...	...	0·025
9	...	...	...	...	0·036
10	...	...	...	0·012	0·050
11	...	...	...	0·018	0·062
12	...	...	...	0·025	0·086
13	...	...	0·010	0·050	0·125
14	...	...	0·012	0·075	0·162
15	..	...	0·025	0·100	0·225
16	...	...	0·050	0·150	0·286
17	...	0·010	0·062	0·200	0·350
18	...	0·012	0·100	0·262	0·436
19	...	0·025	0·150	0·350	0·525
20	...	0·050	0·186	0·425	0·625
21	...	0·075	0·250	0·525	0·750
22	...	0·112	0·300	0·650	0·975
23	...	0·136	0·350	0·775	1·200
24	...	0·175	0·400	0·900	1·436
25	0·010	0·200	0·462	1·025	1·662
26	0·012	0·236	0·512	1·175	1·900
27	0·025	0·262	0·562	1·300	2·125
28	0·036	0·300	0·612	1·436	2·350
29	0·050	0·336	0·675	1·575	2·600
30	0·062	0·362	0·750	1·700	2·812
31	0·100	0·412	0·850	1·812	3·086
32	0·136	0·462	0·950	1·975	3·350
33	0·186	0·512	1·050	2·100	3·625
34	0·225	0·575	1·150	2·236	3·900
35	0·275	0·625	1·250	2·362	4·175
36	0·312	0·675	1·336	2·500	4·450
37	0·350	0·725	1·436	2·625	4·736
38	0·400	0·525	1·536	2·762	5·000
39	0·436	0·836	1·636	2·900	5·275
40	0·486	0·886	1·736	3·025	5·550
41	0·550	0·950	1·850	3·150	5·850
42	0·612	1·050	1·986	3·275	6·125
43	0·686	1·125	2·112	3·412	6·400
44	0·750	1·212	2·250	3·525	6·700
45	0·825	1·300	2·325	3·736	6·975
46	0·886	1·386	2·500	3·825	7·250
47	0·962	1·475	2·636	3·962	7·536
48	1·025	1·512	2·762	4·100	7·825
49	1·100	1·650	2·886	4·236	8·100

3. Acid of spec. grav. 1·633 (say, 71·5 per cent. H_2SO_4).

N_2O_3 originally present. Grams in 1 litre.	Loss of N_2O_3 in grams per litre at				
	50°.	60°.	70°.	80°.	90°.
1	0·012	0·025	0·036	0·100	0·150
2	0·050	0·075	0·086	0·225	0·300
3	0·100	0·150	0·186	0·350	0·436
4	0·162	0·212	0·300	0·536	0·612
5	0·212	0·300	0·436	0·736	0·825
6	0·300	0·425	0·636	1·000	1·112
7	0·400	0·562	0·836	1·275	1·425
8	0·500	0·712	1·036	1·550	1·750
9	0·600	0·835	1·236	1·812	2·062
10	0·700	0·936	1·436	2·086	2·375
11	0·800	1·125	1·636	2·350	2·712
12	0·871	1·262	1·825	2·636	3·075
13	0·986	1·400	2·036	2·900	3·436
14	1·086	1·536	2·225	3·175	3·800
15	1·186	1·675	2·412	3·450	4·162
16	1·275	1·800	2·612	3·725	4·512
17	1·375	1·936	2·786	4·000	4·886
18	1·475	2·036	2·975	4·262	5·236
19	1·562	2·250	3·186	4·550	5·600
20	1·662	2·412	3·400	4·850	5·986
21	1·812	2·612	3·650	5·162	6·400
22	1·975	2·812	3·912	5·512	6·862
23	2·186	3·062	4·250	5·912	7·425
24	2·436	3·336	4·612	6·350	8·036
25	2·700	3·636	5·000	6·800	8·662
26	3·000	3·950	5·412	7·300	9·362
27	3·312	4·300	5·850	7·812	10·150
28	3·662	4·636	6·325	8·400	11·000
29	4·025	5·012	6·812	8·025	11·986
30	4·412	5·412	7·350	9·675	13·125
31	4·800	5·836	7·950	10·386	14·500
32	5·236	6·325	8·575	11·175	16·362

reaction of SO_2 on nitrous sulphuric acid is nothing like so simple as previously assumed. If the acid exceeds the strength of 1·630, the SO_2 does not reduce the N_2O_3 to NO, but forms with it and sulphuric acid nitroso-sulphuric acid, so long as there is oxygen in excess and the atmosphere contains more N_2O_3 than corresponds to the tension of the acid in question at that special temperature (comp. above). Otherwise reduction to NO takes place. Acids below spec. grav. 1·600 are able to fix N_2O_3 under the same conditions, but only at comparatively low temperatures; at higher temperatures there is reduction even in the presence of an excess of O and N_2O_3.

4. Acid of spec. grav. 1·60 (say, 69 per cent. H_2SO_4).

N_2O_3 originally present. Grams in 1 litre.	Loss of N_2O_3 in grams per litre at				
	50°.	60°.	70°.	80°.	90°.
1	0·050	0·086	0·175	0·336	0·412
2	0·100	0·236	0·436	0·725	0·912
3	0·325	0·525	0·775	1·150	1·500
4	0·562	0·836	1·250	1·910	2·100
5	0·812	1·150	1·500	2·120	2·700
6	1·050	1·450	1·900	2·500	3·350
7	1·286	1·800	2·350	3·100	4·112
8	1·512	2·150	2·800	3·725	4·900
9	1·750	2·425	3·250	4·336	5·686
10	1·975	2·812	3·712	4·900	6·475
11	2·250	3·162	4·436	5·265	7·300
12	2·512	3·536	4·675	6·325	8·125
13	2·786	3·936	5·150	7·012	8·962
14	3·065	4·250	5·650	7·700	9·750
15	3·360	4·612	6·125	8·400	10·625
16	3·600	4·975	6·612	9·125	11·462
17	3·862	5·350	7·100	9·525	12·250
18	4·150	5·712	7·600	10·462	13·136
19	4·425	6·075	8·086	11·350	13·975
20	4·700	6·425	8·562	11·850	14·800

Another reducing agent whose action had formerly been overlooked is carbon, in the shape of the *coke* employed for packing the Gay-Lussac tower. I have shown (J. Soc. Chem. Ind. 1885, p. 31) that coke has a very strong reducing-action on nitric acid dissolved in sulphuric acid, which goes far towards explaining the fact that the "nitrous vitriol" from the Gay-Lussac towers never, except under altogether exceptional circumstances, contains any nitric acid, even when considerable quantities of N_2O_4 had been present in the exit gases. But the reduction goes further; some N_2O_3 itself, in the shape of nitroso-sulphuric acid, is by the coke reduced to lower nitrogen oxides and is thus lost. This has been proved by myself in my laboratory (Zeitsch. f. angew. Chem. 1890, p. 195); and as it is a matter of importance, we give the results obtained in the following table (p. 232).

It will be seen that at 40° C. two hours' contact reduced the percentage of N_2O_3 by 2·4 to 4·5 per cent.; at 70° the reduction sometimes went as far as 28 per cent. The latter temperature ought never to occur in a Gay-Lussac tower, but it does occur regularly in Glover towers up to the top. The conclusion is that

Material used.	Temperature. °C.	Time (hours).	Original percentage in N_2O_3, grams.	Percentage decrease	
				in grms. N_2O_3.	of the N_2O_3 originally present.
1. Nitrous Vitriol of spec. grav. 1·8375.					
Gas Coke in lumps	15	24	18·93	0·330	1·71
" "	14	2	18·92	0·539	2·86
" "	70	2	19·30	0·742	3·84
Oven Coke in lumps	15	24	19·30	0·285	1·48
" "	40	2	18·92	0·362	1·91
" "	70	2	19·30	0·452	2·34
Gas Coke in powder	15	24	19·30	0·790	4·09
" "	40	2	18·92	0·858	4·54
" "	70	2	16·22	0·903	5·57
" "	100	2	16·22	4·611	28·43
Oven Coke in powder ...	15	24	19·30	0·379	1·96
" " ...	40	2	18·92	0·451	2·38
" " ...	70	2	16·22	0·527	3·25
" " ...	100	2	16·22	2·770	17·08
2. Nitrous Vitriol of spec. grav. 1·725.					
Gas Coke in powder	15	24	19·50	0·333	1·98
" "	40	2	19·50	0·574	2·94
" "	70	2	19·50	0·891	4·57
" "	100	2	19·50	3·410	17·49

coke packing should be entirely avoided in Glover towers, and that it is not advisable even for Gay-Lussac towers (comp. Chap. VI.).

ANALYSIS OF SULPHURIC ACID.

Qualitatively sulphuric acid is always recognized best by the white precipitate of barium sulphide which it gives with barium chloride, both in the free state and in the solutions of its salts, even when very much diluted. This precipitate mostly settles down as a heavy powder, but in extremely dilute liquids occasionally appears only after some little time as a white cloud. Barium sulphate is as good as insoluble in water, solutions of salts, and free dilute acids; in concentrated acids it is a little soluble, especially on heating, also in concentrated sulphuric acid itself and in solutions of ferric chloride. On the other hand, in a very concentrated liquid free from sulphuric acid, but containing much hydrochloric or, especially, nitric acid, the addition of barium chloride may cause a precipitate of barium chloride itself or of barium nitrate, which, however, is distinguished from barium sulphate by its crystalline appearance, and even more by vanishing on dilution of the liquid; barium seleniate is distinguished from barium sulphate by its solubility on boiling with concentrated hydrochloric acid, and by its behaviour with the blowpipe. The reaction proves the presence of sulphuric acid either in its free state or in its salts. In order to find sulphuric acid in the *free* state in the presence of sulphates of acid reaction, either the alcoholic solution of the substances can be tried with barium chloride (free acid being soluble, but all sulphates insoluble in absolute alcohol), or the charring properties of concentrated oil of vitriol are made use of by evaporating the solution mixed with a little cane-sugar in a small porcelain capsule on the water-bath, and observing whether a blackening of the sugar takes place. This reaction, however, also takes place with the sulphates of very weak bases, such as alumina or ferric oxide; nor can sulphuric acid be distinguished with certainty in this way from hydrochloric or nitric acid; but in phosphoric, acetic, tartaric acid, &c. a very small proportion of sulphuric acid can be proved by this reaction. Another reaction for free sulphuric acid, as well as for any strong free acid, is that with methyl-orange: the latter does not change colour by adding metallic salts, but is changed by the smallest quantity of free sulphuric acid.

In insoluble sulphates the acid is recognized by fusing them with alkaline carbonates, or by boiling with concentrated solutions of the same and filtering the solution of the alkaline sulphate formed thereby from the insoluble carbonates, or with the blowpipe, on charcoal, by the formation of sodium sulphate, according to well-known methods.

The quantitative estimation of free sulphuric acid for technical purposes is almost exclusively effected by volumetric methods or by the hydrometer. In both cases, of course, impurities will have a disturbing action; but for technical purposes they may nearly always be neglected (compare p. 187 *et seq.*). The hydrometric estimation of sulphuric acid has been already described in detail; and we shall here only point out again that the temperature must not be neglected in this case.

The volumetrical estimation of free acid generally takes place by means of a standard solution of potash, soda, or ammonia.

According to the accuracy required, either a normal solution is used (that is, one containing per litre an equivalent expressed in grams), or a semi- or decinormal solution, &c.

Formerly tincture of litmus was most frequently used as indicator. Litmus is not well adapted for working in artificial light: the red appears almost as clear as water, the blue like a dark violet; but the transition from bright red into purple, &c., cannot be seen with certainty. This can be remedied by monochromatic light, if the artificial light be coloured yellow by common salt: the red appears clear as water, the blue like deep black; and the transition is even sharper than in daylight.

Litmus has, moreover, the disadvantage that it is sensitive to all weak acids as well, and that it is destroyed by sulphuretted hydrogen. If, therefore, carbonates are to be tested with it, this must be done at a boiling heat, and the boiling must be prolonged for some time. If any sulphides are present, an excess of acid must be added, and all the H_2S expelled by prolonged boiling; only then should the litmus be added, and the analysis finished by re-titrating. This makes application of litmus very troublesome in alkalimetry; in fact a real error is introduced by the necessity of long boiling, if this is done in glass vessels which yield up some alkali thereby. In acidimetry this drawback is less felt, but only when the standard alkali is kept entirely free from carbonates, which is very difficult in the daily practice of alkali-works.

Phenolphthalein has in many cases taken the place of litmus. It is one of the most sensitive indicators known, and the change from no colour in acid solutions to a decided pink with the faintest trace of free alkali is easily noticed even in artificial light. But this indicator has two drawbacks: it is too sensitive even towards the weakest acids (*e.g.* CO_2), and it fails in the presence of ammonia. The former circumstance entails exactly the same difficulties as in the case of litmus. Hence, while phenolphthalein is the best of all indicators for titrating weak acids, it is decidedly inferior to methyl-orange for the titration of alkalies containing carbonates or sulphides, and in the acidimetry of strong acids.

The indicator which in alkali and acid works is now universally employed is *methyl-orange* *. This is sulphobenzene-azodimethyl-

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* I have proposed this name for the indicator introduced by me, in lieu of the commercial names of Poirrier's Orangé No. III. or helianthin (Chem. News, xliv. p. 288); and it has been generally adopted.

aniline, or the sodium salt of this compound:

$$(SO_3Na)\ C_6H_4-N_2-C_6H_4\,N(CH_3)_2,$$

which is employed in an aqueous solution of 1 in 2000 water, or even more dilute, and a very small quantity of the solution is used for each test. It is best to keep it in a bottle with a perforated cork, a glass tube drawn out to a point and inserted in the cork serving as a pipette for regulating the supply. Methyl-orange is orange in neutral solutions or in the presence of free alkali, but is faintly yellow in very dilute solutions, and no more ought to be added to the liquid to be tested than suffices to colour it just perceptibly yellow. In this case a single drop of fifth-normal sulphuric or hydrochloric acid will cause a transition into red. But when too much of the indicator has been added, so that the colour of the solution is orange, the transition into red (or, rather, in this case into pink) is only gradual, and therefore useless. Warm solutions behave in a similar manner. It is therefore a distinct rule to be observed with methyl-orange, to employ as little as possible of it, and to work always at the ordinary temperature. This is made possible by the fact that methyl-orange is not acted upon by weak acids, such as CO_2, H_2S, acetic acid, &c.; and this is undoubtedly one of its most valuable properties, since the trouble and loss of time in boiling the liquids, and the error introduced in the case of glass vessels, are thereby avoided. Both Na_2CO_3 and $NaHCO_3$ can be titrated directly in the cold just as well as NaOH, the total available soda being always indicated. Sulphurous acid behaves in the manner explained, *suprà* (p. 160), that is, the compound Na_2SO_3 is alkaline, $NaHSO_3$ neutral, to methyl-orange. Oxalic acid, as well as other strong organic acids, come in between sulphurous acid and the strong mineral acids; no sharp results can be obtained with them, and hence oxalic acid cannot serve as standard acid with methyl-orange. On the other hand, ammonia, which cannot be titrated with phenolphthalein, behaves quite normally towards methyl-orange, just like potash and soda. The normal sulphates of peroxide of iron, alumina, &c., which give an acid reaction with litmus, are neutral towards methyl-orange, so that any free acid present with them can be estimated by means of this indicator.

Methyl-orange is destroyed by nitrous acid. Nevertheless it can be easily employed in titrating sulphuric or nitric acid containing nitrous acid in two ways: either by adding the indicator shortly before the saturation is completed and quickly finishing the titration, or by supersaturating the acid with caustic soda and retitrating with standard acid.

Nitrous acid acts upon methyl-orange like a strong mineral acid, and is therefore completely saturated before the pink colour has changed to yellow, if there is not time for the colouring-matter to be destroyed.

The tropæolins, formerly recommended as indicators, are nothing like so sensitive as methyl-orange, and are best not used at all as indicators, especially since several totally distinct compounds are comprised under this name, and the dealers do not always supply that which is really wanted.

Free sulphuric acid (including that contained in commercial ferric or aluminium sulphate, or any other sulphate) is estimated by adding a drop of methyl-orange solution, which causes a pink colour, and then adding a standard solution of alkali, till the pink tint has changed into pure light yellow. It is best to check this by reproducing the faint pink shade by means of a drop of standard acid.

The normal alkaline solution itself is best standardized by means of a normal acid, be it sulphuric or hydrochloric acid; and this on its part is best standardized by pure ignited sodium carbonate, which is easily obtained or prepared—for instance, by washing and igniting sodium bicarbonate. If sodium carbonate, bought as chemically pure, dissolves in water without any residue, and shows by the ordinary reagents no chloride or sulphate, or only unweighable traces of these, it can be used at once for standardizing normal acids after moderately igniting. If methyl-orange be used as indicator, this roundabout way need not be taken, especially at works' laboratories, but pure sodium carbonate itself can be used as acidimetrical liquid, either in a normal solution containing 53 grams per litre or in more dilute solutions. The latter are more to be recommended, since the really normal solution causes efflorescences of sodium carbonate at the lower ends of the burettes, &c., which does not happen with semi-normal or weaker solutions, at least not for some time.

Although it is more important in alkalimetry than in acidimetry, we will here treat of the *standard acid* itself. As such many factory-chemists use sulphuric acid, but we recommend as more suitable hydrochloric acid, both because it can be used for estimating alkaline earths as well, and because it admits of a twofold way of checking the standard, either volumetrically by pure sodium carbonate, or gravimetrically by argentic nitrate. The gravimetric estimation of sulphuric acid by barium chloride is nothing like so accurate as the estimation of HCl in the shape of AgCl. Oxalic acid, most strongly recommended by Mohr, and formerly used by very many chemists, has great drawbacks. It is extremely difficult to prepare in the perfectly pure and dry state, without losing some of the water of crystallization; it does not keep in weak solutions, and it cannot be employed with methyl-orange.

For standardizing normal acids, sometimes a solution of pure sodium carbonate is made, of which portions are taken out with a pipette. For the most accurate estimations it is, however, always preferable to weigh each portion of sodium carbonate, directly after igniting and cooling, into the beaker, since it is never possible to measure as accurately as to weigh, because, among other reasons, the volumetrical apparatus very rarely agree quite accurately one with another. In spite of the trouble, it should most certainly not be neglected to compare, in the first instance, the pipettes with all the measuring-flasks, in order to see whether the former fill the latter precisely ; secondly, to calibrate the burettes accurately, in which case it will often be found that the upper parts differ by several per cent. from the middle and lower parts, and cause a corresponding error. Of course the burettes must again be compared with the other measuring-apparatus.

The standard acid is made to represent *equivalents*, not molecules; that is, if sulphuric or oxalic acid, it will contain one half of the molecular weight in grams, viz. 49 or 63 grams, because these acids are bivalent; but if it is the univalent hydrochloric or nitric acid, it will contain the total molecular weight, viz. 36·46 grams HCl, or 63 grams NO_3H. First of all, the acid is diluted a little less than necessary, and it is found out how many cub. centims. of it are required for a certain quantity of sodium carbonate. From this the quantity of water is computed which is required for obtaining an exactly normal acid; and after mixing this with the acid the accuracy of the standard is ascertained by repeated titrating with sodium carbonate. Not less than 2 to 3 grams of the latter should be taken for each test. If litmus is to be the indicator, to the alkaline solution drops of tincture of litmus are added till it becomes very markedly blue, then acid till strong effervescence sets in; and the liquid is now made to boil; then to the hot liquid gradually more and more acid is added, till the blue colour has passed through the purple and reddish purple of the CO_2 reaction to the bright red of the SO_4H_2 reaction. The liquid cooled by the addition of acid must be constantly heated again. Often, after several minutes' boiling, the apparently red liquid again turns purple and then blue. When working with boiling liquids there is never any doubt, to a single drop, respecting the point where the pure red sets in. The test must be made in a porcelain capsule, not in a glass beaker. Precisely the same troublesome method must be employed with phenolphthalein. All this trouble is saved by using methyl-orange as indicator and working in the cold.

When a perfectly accurate normal acid has been obtained, the normal alkali, whether ammonia, soda, or potash, is most easily made from it; and this is now used for the acidimetric test of sulphuric acid. Concentrated sulphuric acid must, of course, first be diluted in the usual manner.

Analysis of Fuming Oil of Vitriol.

Several communications have been made on this subject, as by Fürstenau (Chemiker-Zeitung, 1880, p. 18), Möller (ibid. p. 569), Becker (ibid. p. 600), Winkler (Chem. Ind. 1880, p. 194), Clar and Gaier (ibid. 1881, p. 251). We shall, in the first instance, principally describe the methods contained in Lunge and Hurter's Alkali-Maker's Hand-book,' as derived from practical information, with a few improvements.

In the present case even the *taking of the sample* is not quite a simple task. Measuring it in a pipette is out of the question, it must be weighed. But even for this purpose the article, if solid, must be first liquefied. This is comparatively easy with partly crystallized acid or with solid pyrosulphuric acid; these can be liquefied without any danger in a closed vessel by gently heating to 30° in a sand-bath. Soldered-up tins are generally placed in a suitably heated stove. There is no sensible loss of strength if the aperture for this purpose is previously opened and at once covered with a watch-glass. This prevents any pressure within the vessel during the heating, which must otherwise be guarded against in opening it. The case is different with products containing a larger percentage of anhydride. These do not liquefy completely, a portion always remaining in the state of a gelatinous residue. This residue is, however, composed exactly like the liquid portion, so that the sample may be taken out of the latter without any danger of making a mistake.

The sample is weighed either in glass bulbs or in a glass tap-tube. The former are very thin bulbs of about ¾ inch diameter, ending each way in a capillary tube (fig. 40). The liquefied acid (2 or 3 grams) is sucked into the bulb, without danger to the operator, by means of a bottle closed with an india-rubber cork, through which passes a tightly-fitting glass tap, connected at its free end with an elastic tube. Suction is applied to the latter, the tap is closed, the elastic tube is drawn over one of the capillary ends of the weighing-bulb, and by opening the tap a sufficient quantity of acid is admitted into the bulb.

Fig. 40.

The capillary tube is cleaned and one of the two ends is sealed at the lamp. The other end can be left open without fear of any loss of SO_3 or attraction of moisture during weighing. The weighing is best done on a small platinum crucible with two nicks, on which the ends of the bulb can rest. If the latter should be accidentally broken, the acid runs into the crucible, not on the balance. Then the bulb, open end downwards, is put into a small Erlenmeyer flask, into the neck of which it should fit exactly (fig. 40), and which contains so much water that the capillary tube dips pretty far into it to prevent any loss of SO_3 on mixing the acid with water. Now break off the other point, allow the acid to run out, squirt a few drops of water into the upper capillary, and ultimately rinse the whole bulb-tube by repeated aspiration of water. Dilute the liquid to 500 c.c. and take 50 c.c. for each test. The testing is done with fifth-normal solution of soda (1 c.c. = 0·008 grm. SO_3) and litmus or methyl-orange as indicator. The acidity found is diminished by that proceeding from SO_2, found by titrating another sample with iodine.

In lieu of the bulb-tube (first proposed by Clar and Gaier) we prefer the glass tap-tube, as shown in fig. 41. The tap should be tight without greasing, and the tube below it should taper gradually. It is charged by suction, in the same way as described above, with about 0·5 grm. of Nordhausen acid, no more, in order to be able to titrate it directly, without taking an aliquot portion. After the proper quantity of acid has been introduced, the tap is closed, the tube is cleaned outside with filtering-paper, and it may be weighed at once, without any fear of a change of weight during the operation. It is, however, preferable to employ a tube (as shown in fig. 42) ground into an outer glass case, which is, of course, tared together with the empty tube.

Fig. 41.

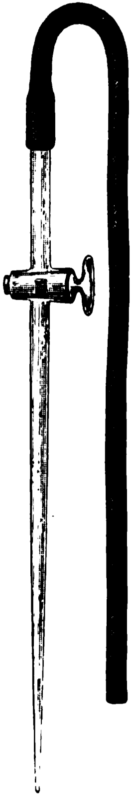


Fig. 42.

After weighing, place the tube point downwards in water, or, in the case of nearly pure anhydride or the strongest Nordhausen acids, in a layer of crystallized, coarsely powdered Glauber's salt, and slowly run out the contents. Then squirt a drop of water from above into the tube, allow it to stand for a moment, and rinse thoroughly with water. Anhydride once melted for the purpose of filling the tube remains liquid enough to complete the weighing and running out without requiring to be heated again.

The most convenient apparatus for weighing off fuming sulphuric acid (as well as other fuming acids or substances evolving vapours) is the "bulb-tap pipette," proposed by Lunge & Rey (Zeitsch. f. angew. Chem. 1891, p. 165), and shown in fig. 42, in which both the filling as well as the weighing and discharging are performed without any loss of vapours and without requiring any special aspirating-apparatus. Above tap *a* there is a bulb *b*, rather less than an inch in diameter, and above this a second tap *c*. The lower portion of the pipette is ground into a glass tube *d*, closed at the bottom. In the conical part of the pipette there is a groove *e*, reaching halfway down, the corresponding half of the groove *f* being in the outer tube. By turning the pipette in the latter, the tube *d* can be made to communicate with the outer air, or the reverse. When the pipette is to be used, close tap *a*, suck at the top with the mouth, and before leaving off shut tap *c*, so that the bulb *b* contains a partial vacuum. Dip the point of the pipette into the acid and open *a*; the acid will rise up, but *a* is shut before it gets so far, or even sooner, when enough has got in. Clean the pipette outside, put it into *d*, and weigh. In most ordinary cases (with other acids, ammonia, &c.) the grooves *e* and *f* are made to communicate; water is squirted through *c* into *b* and then run through *a*, with the contents of the pipette, into *d*, the air escaping through *e* and *f*. The dilute acid is run into a beaker and titrated. In the case of Nordhausen acid it is preferable to take the pipette out of *d*, rinse the latter into a beaker, run the contents of the pipette, by opening *a*, into water or Glauber's salt contained in the same beaker, then squirt water through *c* (during which time *a* may be closed), and rinse the pipette into the same beaker. The sucking at *c* is quite sufficient to produce the necessary rarefaction of air in *b*, and no vapours are lost, as is inevitable with any other kind of aspiration.

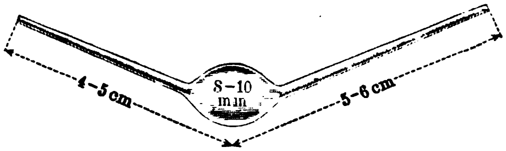
Very strong oleum (70 per cent. SO_3 and upwards) is best weighed in glass bulbs (p. 239) sealed at both ends; these are put into a bottle containing sufficient water, which is closed by a

ground-in stopper; the bulb is smashed by shaking the bottle, and the titration is made.

The sampling of *solid* sulphuric anhydride is not an easy matter. This substance, which is now a regular article of trade and is sent out in iron bottles, is much too compact and tough to enable a sample to be taken out by means of an auger. Before using it, it is always heated in a stove till it has completely liquefied; but in this state the bottle on opening emits such a dense cloud of fumes that any sampling is out of the question. The way out of the difficulty is this:—In a stoppered bottle some lumps of the solid anhydride are weighed off on a large balance and are then mixed with a sufficient quantity of accurately analyzed monohydrated sulphuric acid, to form an acid of 70 per cent. SO_3, which is liquid at ordinary temperatures. The solution is promoted by gently heating the bottles, say to 30° or 40° C., with the stopper loosely put on. At last a sample is taken out by means of the pipette described above (p. 240) and the analysis performed in the usual way, taking account of the slight proportion of water present in the "monohydrate" employed.

Rosenlecher (Zeitsch. anal. Ch. xxxvii. p. 209) describes the method employed at Freiberg. A number of bulbs are made from a glass tube, 6 or 8 mm. wide, of the form shown in fig. 43, and keeping them exactly to the dimensions indicated. The capillary ends are contracted before a spirit-lamp to ½ mm. bore, in the case of very strong anhydride to ¼ mm. The bulbs are filled by aspiration by means of a capillary rubber tube drawn over the shorter end, in case of need interposing a test-tube filled with soda crystals. The suction is continued until the acid arrives in the bulbs before the heavy fumes enter the shorter capillary. All the bulbs are turned with the points of the capillaries upwards, cleaned outside, and placed in a paste-board box provided with nicks. The weighing is performed in a platinum crucible (p. 239) or on a specially made wire stand. No attraction of moisture need be feared during the

Fig. 43.



weighing, but the bulbs must not be heated by touching them with the fingers. They are then placed in bottles, charged with 20 or 30 c.c. water of ordinary temperature and the indicator, in such manner that the acid does not flow out. The wetted stopper is put tightly in, the bottles are placed sideways (up to this time the colour of the indicator should not have changed), the bulbs broken by shaking, and then, after the white fumes have vanished, the titration is performed in the bottle itself.

The results of titration are first calculated for the total (combined and uncombined with water) SO_3, each c. c. of normal soda solution indicating 0·040 grm. SO_3, and the proportion of free SO_3 and H_2SO_4 present is then read off by means of the following formula: $SO_3 = S - 4{\cdot}444\ (100 - S)$, in which SO_3 denotes the free sulphur trioxide, and S the total SO_3 as found by titration.

This calculation is saved by the following table, computed by Knietsch (Ber. 1901, p. 4114):—

SO_3		SO_3		SO_3		SO_3		SO_3		SO_3		SO_3	
Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.
81·63	0·0	84·3	14·5	87·0	29·2	89·6	43·4	92·2	57·5	94·8	71·7	97·4	85·8
81·7	0·4	84·4	15·1	87·1	29·8	89·7	43·9	92·3	58·1	94·9	72·2	97·5	86·4
81·8	0·9	84·5	15·6	87·2	30·3	89·8	44·5	92·4	58·6	95·0	72·8	97·6	86·9
81·9	1·5	84·6	16·2	87·3	30·9	89·9	45·0	92·5	59·2	95·1	73·3	97·7	87·5
82·0	2·0	84·7	16·7	87·4	31·4	90·0	45·6	92·6	59·7	95·2	73·9	97·8	88·0
82·1	2·6	84·8	17·2	87·5	31·9	90·1	46·1	92·7	60·3	95·3	74·4	97·9	88·6
82·2	3·1	84·9	17·8	87·6	32·5	90·2	46·6	92·8	60·8	95·4	75·0	98·0	89·1
82·3	3·6	85·0	18·3	87·7	33·0	90·3	47·2	92·9	61·3	95·5	75·5	98·1	89·7
82·4	4·2	85·1	18·9	87·8	33·6	90·4	47·7	93·0	61·9	95·6	76·1	98·2	90·2
82·5	4·7	85·2	19·4	87·9	34·1	90·5	48·3	93·1	62·4	95·7	76·6	98·3	90·7
82·6	5·3	85·3	20·0	88·0	34·7	90·6	48·8	93·2	63·0	95·8	77·1	98·4	91·3
82·7	5·8	85·4	20·5	88·1	35·2	90·7	40·4	93·3	63·5	95·9	77·7	98·5	91·8
82·8	6·4	85·5	21·0	88·2	35·8	90·8	49·9	93·4	64·1	96·0	78·3	98·6	92·4
82·9	6·9	85·6	21·6	88·3	36·3	90·9	50·5	93·5	64·6	96·1	78·8	98·7	92·9
83·0	7·5	85·7	22·2	88·4	36·8	91·0	51·0	93·6	65·2	96·2	79·3	98·8	93·5
83·1	8·0	85·8	22·7	88·5	37·4	91·1	51·6	93·7	65·7	96·3	79·9	98·9	94·0
83·2	8·5	85·9	23·2	88·6	37·9	91·2	52·1	93·8	66·2	96·4	80·4	99·0	94·6
83·3	9·1	86·0	23·8	88·7	38·5	91·3	52·6	93·9	66·8	96·5	81·0	99·1	95·1
83·4	9·6	86·1	24·3	88·8	39·0	91·4	53·2	94·0	67·3	96·6	81·5	99·2	95·6
83·5	10·2	86·2	24·9	88·9	39·6	91·5	53·7	94·1	67·9	96·7	82·0	99·3	96·2
83·6	10·7	86·3	25·4	89·0	40·1	91·6	54·3	94·2	68·4	96·8	82·6	99·4	96·7
83·7	11·3	86·4	26·0	89·1	40·6	91·7	54·8	94·3	69·0	96·9	83·1	99·5	97·3
83·8	11·8	86·5	26·5	89·2	41·2	91·8	55·4	94·4	69·5	97·0	83·7	99·6	97·8
83·9	12·3	86·6	27·0	89·3	41·7	91·9	55·9	94·5	70·1	97·1	84·2	99·7	98·4
84·0	12·9	86·7	27·6	89·4	42·3	92·0	56·4	94·6	70·6	97·2	84·8	99·8	98·9
84·1	13·4	86·8	28·1	89·5	42·8	92·1	57·0	94·7	71·2	97·3	85·3	99·9	99·5
84·2	14·0	86·9	28·7										

ground-in stopper; the bulb is smashed by shaking the bottle, and the titration is made.

The sampling of *solid* sulphuric anhydride is not an easy matter. This substance, which is now a regular article of trade and is sent out in iron bottles, is much too compact and tough to enable a sample to be taken out by means of an auger. Before using it, it is always heated in a stove till it has completely liquefied; but in this state the bottle on opening emits such a dense cloud of fumes that any sampling is out of the question. The way out of the difficulty is this:—In a stoppered bottle some lumps of the solid anhydride are weighed off on a large balance and are then mixed with a sufficient quantity of accurately analyzed monohydrated sulphuric acid, to form an acid of 70 per cent. SO_3, which is liquid at ordinary temperatures. The solution is promoted by gently heating the bottles, say to 30° or 40° C., with the stopper loosely put on. At last a sample is taken out by means of the pipette described above (p. 240) and the analysis performed in the usual way, taking account of the slight proportion of water present in the "monohydrate" employed.

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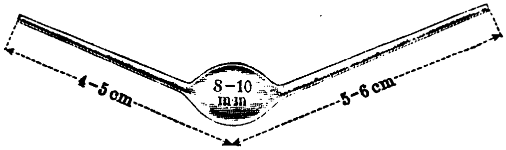
Fig. 43.



weighing, but the bulbs must not be heated by touching them with the fingers. They are then placed in bottles, charged with 20 or 30 c.c. water of ordinary temperature and the indicator, in such manner that the acid does not flow out. The wetted stopper is put tightly in, the bottles are placed sideways (up to this time the colour of the indicator should not have changed), the bulbs broken by shaking, and then, after the white fumes have vanished, the titration is performed in the bottle itself.

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Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.
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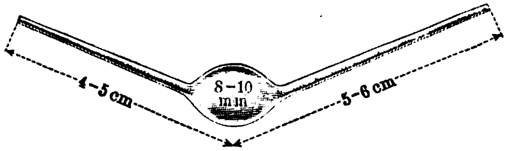
81·8	0·9	84·5	15·6	87·2	30·3	89·8	44·5	92·4	58·6	95·0	72·8	97·6	86·9
81·9	1·5	84·6	16·2	87·3	30·9	89·9	45·0	92·5	59·2	95·1	73·3	97·7	87·5
82·0	2·0	84·7	16·7	87·4	31·4	90·0	45·6	92·6	59·7	95·2	73·9	97·8	88·0
82·1	2·6	84·8	17·2	87·5	31·9	90·1	46·1	92·7	60·3	95·3	74·4	97·9	88·6
82·2	3·1	84·9	17·8	87·6	32·5	90·2	46·6	92·8	60·8	95·4	75·0	98·0	89·1
82·3	3·6	85·0	18·3	87·7	33·0	90·3	47·2	92·9	61·3	95·5	75·5	98·1	89·7
82·4	4·2	85·1	18·9	87·8	33·6	90·4	47·7	93·0	61·9	95·6	76·1	98·2	90·2
82·5	4·7	85·2	19·4	87·9	34·1	90·5	48·3	93·1	62·4	95·7	76·6	98·3	90·7
82·6	5·3	85·3	20·0	88·0	34·7	90·6	48·8	93·2	63·0	95·8	77·1	98·4	91·3
82·7	5·8	85·4	20·5	88·1	35·2	90·7	49·4	93·3	63·5	95·9	77·7	98·5	91·8
82·8	6·4	85·5	21·0	88·2	35·8	90·8	49·9	93·4	64·1	96·0	78·3	98·6	92·4
82·9	6·9	85·6	21·6	88·3	36·3	90·9	50·5	93·5	64·6	96·1	78·8	98·7	92·9
83·0	7·5	85·7	22·2	88·4	36·8	91·0	51·0	93·6	65·2	96·2	79·3	98·8	93·5
83·1	8·0	85·8	22·7	88·5	37·4	91·1	51·6	93·7	65·7	96·3	79·9	98·9	94·0
83·2	8·5	85·9	23·2	88·6	37·9	91·2	52·1	93·8	66·2	96·4	80·4	99·0	94·6
83·3	9·1	86·0	23·8	88·7	38·5	91·3	52·6	93·9	66·8	96·5	81·0	99·1	95·1
83·4	9·6	86·1	24·3	88·8	39·0	91·4	53·2	94·0	67·3	96·6	81·5	99·2	95·6
83·5	10·2	86·2	24·9	88·9	39·6	91·5	53·7	94·1	67·9	96·7	82·0	99·3	96·2
83·6	10·7	86·3	25·4	89·0	40·1	91·6	54·3	94·2	68·4	96·8	82·6	99·4	96·7
83·7	11·3	86·4	26·0	89·1	40·6	91·7	54·8	94·3	69·0	96·9	83·1	99·5	97·3
83·8	11·8	86·5	26·5	89·2	41·2	91·8	55·4	94·4	69·5	97·0	83·7	99·6	97·8
83·9	12·3	86·6	27·0	89·3	41·7	91·9	55·9	94·5	70·1	97·1	84·2	99·7	98·4
84·0	12·9	86·7	27·6	89·4	42·3	92·0	56·4	94·6	70·6	97·2	84·8	99·8	98·9
84·1	13·4	86·8	28·1	89·5	42·8	92·1	57·0	94·7	71·2	97·3	85·3	99·9	99·5
84·2	14·0	86·9	28·7										

ground-in stopper; the bulb is smashed by shaking the bottle, and the titration is made.

The sampling of *solid* sulphuric anhydride is not an easy matter. This substance, which is now a regular article of trade and is sent out in iron bottles, is much too compact and tough to enable a sample to be taken out by means of an auger. Before using it, it is always heated in a stove till it has completely liquefied; but in this state the bottle on opening emits such a dense cloud of fumes that any sampling is out of the question. The way out of the difficulty is this:—In a stoppered bottle some lumps of the solid anhydride are weighed off on a large balance and are then mixed with a sufficient quantity of accurately analyzed monohydrated sulphuric acid, to form an acid of 70 per cent. SO_3, which is liquid at ordinary temperatures. The solution is promoted by gently heating the bottles, say to 30° or 40° C., with the stopper loosely put on. At last a sample is taken out by means of the pipette described above (p. 240) and the analysis performed in the usual way, taking account of the slight proportion of water present in the "monohydrate" employed.

Rosenlecher (Zeitsch. anal. Ch. xxxvii. p. 209) describes the method employed at Freiberg. A number of bulbs are made from a glass tube, 6 or 8 mm. wide, of the form shown in fig. 43, and keeping them exactly to the dimensions indicated. The capillary ends are contracted before a spirit-lamp to ½ mm. bore, in the case of very strong anhydride to ¼ mm. The bulbs are filled by aspiration by means of a capillary rubber tube drawn over the shorter end, in case of need interposing a test-tube filled with soda crystals. The suction is continued until the acid arrives in the bulbs before the heavy fumes enter the shorter capillary. All the bulbs are turned with the points of the capillaries upwards, cleaned outside, and placed in a paste-board box provided with nicks. The weighing is performed in a platinum crucible (p. 239) or on a specially made wire stand. No attraction of moisture need be feared during the

Fig. 43.



weighing, but the bulbs must not be heated by touching them with the fingers. They are then placed in bottles, charged with 20 or 30 c.c. water of ordinary temperature and the indicator, in such manner that the acid does not flow out. The wetted stopper is put tightly in, the bottles are placed sideways (up to this time the colour of the indicator should not have changed), the bulbs broken by shaking, and then, after the white fumes have vanished, the titration is performed in the bottle itself.

The results of titration are first calculated for the total (combined and uncombined with water) SO_3, each c. c. of normal soda solution indicating 0·040 grm. SO_3, and the proportion of free SO_3 and H_2SO_4 present is then read off by means of the following formula: $SO_3 = S - 4{\cdot}444\ (100 - S)$, in which SO_3 denotes the free sulphur trioxide, and S the total SO_3 as found by titration.

This calculation is saved by the following table, computed by Knietsch (Ber. 1901, p. 4114):—

SO_3		SO_3		SO_3		SO_3		SO_3		SO_3		SO_3	
Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.
81·63	0·0	84·3	14·5	87·0	29·2	89·6	43·4	92·2	57·5	94·8	71·7	97·4	85·8
81·7	0·4	84·4	15·1	87·1	29·8	89·7	43·9	92·3	58·1	94·9	72·2	97·5	86·4
81·8	0·9	84·5	15·6	87·2	30·3	89·8	44·5	92·4	58·6	95·0	72·8	97·6	86·9
81·9	1·5	84·6	16·2	87·3	30·9	89·9	45·0	92·5	59·2	95·1	73·3	97·7	87·5
82·0	2·0	84·7	16·7	87·4	31·4	90·0	45·6	92·6	59·7	95·2	73·9	97·8	88·0
82·1	2·6	84·8	17·2	87·5	31·9	90·1	46·1	92·7	60·3	95·3	74·4	97·9	88·6
82·2	3·1	84·9	17·8	87·6	32·5	90·2	46·6	92·8	60·8	95·4	75·0	98·0	89·1
82·3	3·6	85·0	18·3	87·7	33·0	90·3	47·2	92·9	61·3	95·5	75·5	98·1	89·7
82·4	4·2	85·1	18·9	87·8	33·6	90·4	47·7	93·0	61·9	95·6	76·1	98·2	90·2
82·5	4·7	85·2	19·4	87·9	34·1	90·5	48·3	93·1	62·4	95·7	76·6	98·3	90·7
82·6	5·3	85·3	20·0	88·0	34·7	90·6	48·8	93·2	63·0	95·8	77·1	98·4	91·3
82·7	5·8	85·4	20·5	88·1	35·2	90·7	49·4	93·3	63·5	95·9	77·7	98·5	91·8
82·8	6·4	85·5	21·0	88·2	35·8	90·8	49·9	93·4	64·1	96·0	78·3	98·6	92·4
82·9	6·9	85·6	21·6	88·3	36·3	90·9	50·5	93·5	64·6	96·1	78·8	98·7	92·9
83·0	7·5	85·7	22·2	88·4	36·8	91·0	51·0	93·6	65·2	96·2	79·3	98·8	93·5
83·1	8·0	85·8	22·7	88·5	37·4	91·1	51·6	93·7	65·7	96·3	79·9	98·9	94·0
83·2	8·5	85·9	23·2	88·6	37·9	91·2	52·1	93·8	66·2	96·4	80·4	99·0	94·6
83·3	9·1	86·0	23·8	88·7	38·5	91·3	52·6	93·9	66·8	96·5	81·0	99·1	95·1
83·4	9·6	86·1	24·3	88·8	39·0	91·4	53·2	94·0	67·3	96·6	81·5	99·2	95·6
83·5	10·2	86·2	24·9	88·9	39·6	91·5	53·7	94·1	67·9	96·7	82·0	99·3	96·2
83·6	10·7	86·3	25·4	89·0	40·1	91·6	54·3	94·2	68·4	96·8	82·6	99·4	96·7
83·7	11·3	86·4	26·0	89·1	40·6	91·7	54·8	94·3	69·0	96·9	83·1	99·5	97·3
83·8	11·8	86·5	26·5	89·2	41·2	91·8	55·4	94·4	69·5	97·0	83·7	99·6	97·8
83·9	12·3	86·6	27·0	89·3	41·7	91·9	55·9	94·5	70·1	97·1	84·2	99·7	98·4
84·0	12·9	86·7	27·6	89·4	42·3	92·0	56·4	94·6	70·6	97·2	84·8	99·8	98·9
84·1	13·4	86·8	28·1	89·5	42·8	92·1	57·0	94·7	71·2	97·3	85·3	99·9	99·5
84·2	14·0	86·9	28·7										

This table serves also for the frequently performed operation of mixing Nordhausen acid of a certain percentage of SO_3 with concentrated sulphuric acid in order to produce an acid with a smaller percentage of SO_3. This can be done by means of a formula given by Gerster (Chem. Zeit. 1887, p. 3),

$$x = 100 \frac{b-a}{a-c},$$

where x represents the quantity of sulphuric acid which must be added to 100 parts of the Nordhausen acid; a the total sulphur trioxide in 100 parts of the acid desired; b the total SO_3 in 100 parts of the Nordhausen acid to be diluted; c the total SO_3 in 100 parts of the ordinary acid to be used for diluting. The values of a and b are taken from the preceding table; c is easily calculated by multiplying the percentage of H_2SO_4 with $\frac{80}{98}$ or 0·816. An example will make this clearer. Supposing there is a Nordhausen acid of 25·5 per cent. SO_3 in stock, as well as sulphuric acid of 98·2 per cent. H_2SO_4, and an acid of 19 per cent. SO_3 is required, we have then:

$$a = 85{\cdot}1\ ;\ b = 86{\cdot}3;\ c = 98 \times 0{\cdot}816 = 80{\cdot}1,$$

$$x = 100\,\frac{b-a}{a-c} = 100\,\frac{86{\cdot}3 - 85{\cdot}1}{85{\cdot}1 - 80{\cdot}1} = \frac{120}{5} = 24.$$

That is: by mixing 100 parts of acid of 25·5 per cent. SO_3 with 24 parts of sulphuric acid of 98·2 per cent. H_2SO_4, Nordhausen acid is obtained containing 19 per cent. SO_3. [In reality the strength of the mixed product will be slightly below that calculated, as a certain loss of SO_3 is hardly avoidable in the manipulation.]

In Zsch. f. angew. Chem. 1895, p. 221, I have drawn attention to the fact that in allowing for the SO_2 sometimes a serious mistake is committed. The SO_2 is always tested for by iodine solution, and is then subtracted from the total acidity. Here we must consider that the neutrality-point in the case of phenolphthalein is reached when 1 SO_2 has been combined with 2 NaOH, but in the case of methyl-orange only 1 NaOH is consumed for 1 SO_2. Litmus cannot be used at all, as it gives uncertain results between these two limits. With methyl-orange 1 c.c. normal soda solution indicates 0·040 gram SO_3, but 0·064 gram SO_2. Hence for each c.c. of decinormal iodine solution only 0·05 c.c. of normal or 0·1 c.c. of semi-normal solution of NaOH must be deducted. If this is overlooked, a very serious mistake is committed; for since everything which is not present as SO_3 or SO_2 is assumed to be water, the incorrect allowance for SO_2 will cause not merely a deficiency of SO_3, but a surplus of H_2O; and as this must be represented as combined with 4·444 its weight of water, far too little free SO_3 is found.

A practical instance will illustrate this. 3·5662 grams fuming acid were diluted to 500 c.c., and 100 c.c. (=0·71124 gram) employed for each test. This consumed 5·40 c.c. iodine solution, =5·40×0·0032=0·01728 gram SO_2 or 2·43 per cent. SO_2. On titrating with seminormal soda solution and methyl-orange, 34·40 c.c. was used. By erroneously deducting 0·2×5·40=1·08 c.c., there remained 33·32 c.c.=0·6664 gram SO_3 or 93·70 per cent. The fuming acid therefore would have contained 93·70 per cent. SO_3, 2·43 SO_2, 3·87 H_2O. The 3·87 H_2O is =17·20 SO_3, and the *free* SO_3 would be =93·70−17·20 =76·50 per cent.

In reality the 5·40 c.c. decinormal iodine corresponds to only 0·54 c.c. seminormal soda, leaving 32·86 c.c.=0·6772 gram SO_3=95·21 per cent. Composition of the acid : 95·21 per cent. SO_3, 2·43 SO_3, 2·36 H_2O. The 2·36 H_2O is =10·49 SO_3, leaving 95·21 − 10·49=84·72 per cent. free SO_3. Hence by that erroneous calculation the factory committed an error of 8·25 per cent. to its own disadvantage!

Exactly the same result is obtained when performing the calculation by means of the above table.

We have, as already mentioned, assumed everything as H_2O which has not been found to be present as SO_3 and SO_2. But it is advisable to estimate the *fixed impurities* as well, since otherwise their weight, multiplied by 4·444, is erroneously deducted from the free SO_3.

Setlik (Chemiker-Zeitung, 1889, p. 1670) proposes to substitute the following method for the titration of Nordhausen acid by caustic-soda solution :—50 or 100 grms. are weighed out in a long-necked flask, and water is dropped in very slowly from a burette, divided into $\frac{1}{10}$ c.c., till the fuming has ceased. During the operation the flask must be well cooled. In order to observe the finishing point, the flask must be agitated after adding each drop of water till the fumes have been entirely absorbed by the acid. When no fumes whatever are formed at the surface and a drop, falling into the middle of the acid, dissolves quietly, the end is reached. Acid of more than 35 per cent. SO_3 must be previously diluted with monohydrated sulphuric acid. It is claimed that this plan is much more expeditious and quite as exact as the alkalimetrical way; but the analytical proofs adduced by Setlik himself do not bear this out (there are deviations up to 0·9 per cent. SO_3), and we can regard his method only as a test for individual use, but not between buyer and seller.

Rabe (Chem.-Zeit. 1901, p. 345) estimates the strength of fuming (or ordinary) sulphuric acid by utilizing the fact that Nordhausen acid loses its property of fuming in contact with air as soon as all its SO_3 has been converted into SO_4H_2 by the water present in ordinary sulphuric acid containing less than 100 per cent. SO_4H_2:

$$\begin{aligned} &a\ H_2SO_4 + c\ H_2O + b\ H_2SO_4 + c\ SO_4 \\ &= a\ H_2SO_4 + b\ H_2SO_4 + c\ H_2SO_4. \end{aligned}$$

We require, to begin with, to know the percentage of a certain sample of strong chemically pure sulphuric acid, say 95 per cent. H_2SO_4 + 5 per cent. H_2O, which is ascertained in the usual way by titration. This acid we run from a glass-tap burette into a beaker containing 25 c.c. of Nordhausen acid, repeatedly agitating and blowing upon the acid (cooling is generally unnecessary), until the acid in the beaker does not form any more fumes on shaking. Suppose we require for this 24·8 c c. of the acid *A*, containing 95 per cent. H_2O and 5 per cent. H_2O. If we wish to ascertain the strength of another sample (*B*) of concentrated ordinary acid, we run this from a burette into 25 c.c. of the same Nordhausen acid as before. Suppose we now require 30·5 c.c. of acid *B*; this proves that acid *B* contains $\frac{24{\cdot}8 \times 5}{30{\cdot}5} = 4{\cdot}07$ per cent. H_2O. If no impurities were present, this would mean a strength of 95·93 per cent. H_2SO_4.

On the other hand, the percentage of SO_3 in Nordhausen acid can be ascertained as follows:—Starting with *pure* (say, 30 per cent.) Nordhausen acid (*C*), we run in concentrated ordinary acid *D*, and find that 59·4 c.c. of acid *D* is required to make the fuming of 25 c.c. acid *C* disappear. We now try an unknown Nordhausen acid *E*, and find that 25 c.c. of it require 49·8 c.c. acid *D*. This gives us the proportion $30 : 59{\cdot}4 = x : 49{\cdot}8$ for the percentage of free SO_3 in acid *E*; $x = \frac{30 + 49{\cdot}8}{59{\cdot}4} = 25{\cdot}15$ per cent. SO_3. 1 c.c. of acid *D* had indicated $\frac{30}{59{\cdot}4} = 0{\cdot}505$ per cent. free SO_3; hence we need only multiply the c.c. of acid *D* required for suppressing the fumes of 25 c.c. of any unknown Nordhausen acid by the same coefficient, viz. 0·505.

[Rabe's method yields very quick results, and is probably quite suitable for rough tests in the ordinary routine of acid-making. There is no weighing, only measuring, and any colour or opacity of the acids does not interfere with the test. But as the difference of specific gravities is neglected, this forms an element of uncertainty, and this is greatly increased by the evident difficulty of keeping a stock of exactly analyzed and chemically pure concentrated and Nordhausen acid without any change. As commercial acids always contain certain impurities, these influence the results as well. The only real advantages of this method over that of Setlik are that no cooling is required during the operation, and that the large amount of concentrated acid is more accurately read off than the small amount of water, but otherwise Setlik's method is preferable.]

Nordhausen acid is always sold by the percentage of uncombined sulphuric anhydride it contains (not taking any account of the pyrosulphuric acid, which is considered $= SO_3 + H_2SO_4$). Thus "30 per cent. Nordhausen acid" means a mixture of 30 parts by weight of SO_3 with 70 parts of H_2SO_4. The price of SO_3 is relatively higher in weak than in strong acids, as in manufacturing it the 5 or more per cent. of water contained in ordinary "rectified oil of vitriol" must be saturated with SO_3, each part of water requiring 4·444 parts of SO_3 to form H_2SO_4. It is therefore decidedly more advantageous to dilute strong Nordhausen acid with the strongest obtainable rectified O.V., or still better with monohydrated sulphuric acid.

The estimation of sulphuric acid in *sulphates* has been described, pp. 64 *et seq.*

Estimation of the Impurities of Sulphuric Acid.

The impurities of sulphuric acid are recognizable *qualitatively* in the following manner :—A *residue* on evaporating sulphuric acid in a platinum crucible may contain sulphates of sodium (more rarely of potassium), of calcium, aluminium, iron, lead; copper, zinc, or other metals occur rarely in sensible quantity. *Ammonium* sulphate is sometimes present in somewhat large quantities (Gintl, Chem.-Zeit. 1879, p. 653). The individual substances are sought for by the ordinary analytical methods. *Iron* is already betrayed by the colour of the residue after ignition, and can also be detected in the acid itself, without evaporating it, by the ordinary reagents, such as potassium ferrocyanide, potassium sulphocyanide, &c. *Lead* is often shown as a white precipitate of sulphate on diluting concentrated vitriol with water—further, by adding one or two drops of hydrochloric acid, by which white clouds are formed, which vanish on addition of more hydrochloric acid or on heating; with more certainty it is shown by diluting (even weaker acid) with three or four times its volume of strong alcohol. The precipitate must, of course, be examined further—for instance, with the blowpipe, by reduction on charcoal to metallic lead, by moistening with ammonium sulphide (which blackens it), &c.

Arsenic is recognized by sulphuretted hydrogen in a dilute solution, more safely by Reinsch's test—diluting with equal volumes of water and pure hydrochloric acid, and immersing a bright copper foil, which, after gentle heating, is covered with a fast-adhering slate-grey precipitate, which, according to Lippert, is a compound of copper and arsenic, Cu_6As_2 (if the arsenic is present as arsenic acid, the reaction only sets in after longer heating); further, by Marsh's apparatus, in which, by means of pure zinc and water, the arsenic is given off as arseniuretted hydrogen, and is proved by reduction in a red-hot tube (Berzelius), or by lighting the gas and holding a piece of porcelain in the flame, on which any arsenic appears as spots. Since it is difficult to procure zinc absolutely free from arsenic, it is well to substitute aluminium foil for it. There may be arsenic acid as well as arsenious acid present; this can be proved by neutralizing with ammonia and adding magnesia mixture: any precipitate must contain the arsenic acid, the filtrate the arsenious acid.

Selmi (Gazz. Chimica, x. p. 40) asserts that arsenic can be detected in acid which gives no reaction by Marsh's test, by adding to 1000 grams of the acid 300 grams water and some lead chloride, distilling and testing the first portions of the distillate with sulphuretted hydrogen.

Seybel and Wikander (Chem.-Zeit. 1902, p. 50) prove the presence of arsenic in sulphuric or hydrochloric acid by the yellow precipitate of AsJ_3, produced by the addition of a solution of potassium iodide. Sulphuric acid should be diluted to 45° B., hydrochloric acid should be employed in the concentrated state. The reaction is interfered with by free chlorine, ferric salts, nitrous acid (which equally cause a yellow coloration by the formation of free iodine), and by lead, which forms yellow PbJ_2. (Unfortunately commercial acids mostly contain one or the other of these impurities.)

The Committee of the Society of Chemical Industry, and of the Society of Public Analysts, in 1901, recommend the Marsh-Berzelius test as the most reliable and sensitive, being capable of recognizing 1 part As in 7 millions. Their detailed prescriptions refer more particularly to the detection and appropriate valuation of arsenic in beer and food-materials (Journ. Soc. Chem. Ind. 1902, pp. 94 *et seq.*).

Of volatile substances sulphuric acid may contain:—*hydrochloric acid* (from the common salt present in the nitrate of soda), to be proved by nitrate of silver, after having diluted the acid, silver sulphate being also very soluble; *hydrofluoric acid,* to be proved by heating in a platinum dish covered by a glass plate coated with wax and containing scratched-in figures; *sulphurous acid,* to be proved by the decolorization of a weakly blue solution of iodized starch, or very accurately by reduction with zinc or aluminium to sulphuretted hydrogen, which is recognized by its turning lead-paper brown or by colouring purple an alkaline solution of sodium nitroprusside (comp. pp. 159 *et seq.*). The *oxygen compounds of nitrogen* are nearly always present in the sulphuric acid of trade. They are recognized in the simplest manner, and with nearly as much precision as by any other test, either by the decolorization of a drop of dilute solution of indigo on heating, or by carefully pouring a solution of ferrous sulphate on the acid contained in a test-tube, so that the liquids do not get mixed. In the presence of traces of nitrous acids or of higher nitrogen oxides a brown ring will be formed at the point of contact; if more be present, the iron solution is coloured brown or black;

but after some time it loses colour again, especially if it has become warm by the reaction. Selenium also gives a red ring similar to that given by traces of nitrogen oxides; but the colour, instead of gradually vanishing, after standing for a time turns into a red precipitate at the bottom of the test-tube. Nitrous and hyponitric acids are also recognized by turning blue a solution of starch containing potassium iodide.

The most sensitive reagent for nitrogen acids is *diphenylamine*, which is most conveniently employed in a solution of 0·5 grm. in 100 c.c. concentrated sulphuric acid, diluted with about 20 c.c. of water. A few c.c. of this solution is poured into a test-tube or conical glass, and the solution to be tested is carefully poured on the top, so that the liquids mix only gradually. If traces of nitrogen acids are present, a fine blue colour is produced at the point of contact. But as all other oxidizing substances, also selenious acid, produce the same blue colour, errors may occur through the (very frequent) presence of selenium, which gives the blue reaction with diphenylamine even in the absence of any trace of nitrogen acids. It is therefore necessary to test first with ferrous sulphate, as described above.

As I have shown in Zsch. f. angew. Chem. 1894, p. 345, the diphenylamine reaction is best employed in the following manner: 0·5 gram white diphenylamine is dissolved in 100 c.c. pure strong sulphuric acid, adding 20 c.c. water; the heat assists in dissolving the substance, and the reagent keeps in well-stoppered bottles a long time without turning brown. When testing for nitrogen acids, pour a few c.c. of the specifically heavier liquid into a test-tube and carefully pour the specifically lighter liquid on the top, so that the layers only gradually mix. The presence of as little as $\frac{1}{20}$ milligram nitrogen in the shape of nitrogen acids per litre is indicated by a blue ring forming at the surface of contact of both liquids, most easily perceived by holding the glass sideways against a white background. Both nitric and nitrous acid are indicated in this way.

Brucine indicates only nitric acid if there is a great excess of strong sulphuric acid present; neither selenium nor nitrous acid interfere with this test, but nitrous acid equally reacts with brucine if there is but little sulphuric acid and much water present, say 1: 2. In order to detect nitric acid by itself, an aqueous solution to be tested should contain at least $\frac{2}{3}$ of its volume of strong sulphuric acid. The brucine can be added either as powder or dissolved in pure strong sulphuric acid, say 1 c.c. of a solution of 0·2 gram brucine in 100 c.c. strong acid, for 50 c.c. of the solution to be tested, of which $\frac{3}{4}$ must consist of strong sulphuric acid. If as little as $\frac{1}{100}$ milligram nitric nitrogen be present, a pink colour is produced which gradually, on heating very quickly, passes through orange into yellow. In Zschr. f. angew. Chem. 1894, p. 347, I have shown how this test can be utilized for a quantitative colorimetric estimation of small quantities of nitric acid. Comp. also *ibidem*, 1902, pp. 1, 170, and 241.

Most reagents, like diphenylamine, ferrous sulphate, and indigo, indicate both nitric and nitrous acid. There are far more reagents which prove the presence of *nitrous acid* (or nitrites) *alone*, not that of nitric acid: for instance, a mixture of starch solution with a solution of iodide of zinc (a blue colour being produced), and of various organic amines, which with nitrous acid form corresponding azo-colours (Griess, Berl. Ber. xi. p. 624). Of these the most frequently used are: metaphenylene diamine, which produces a yellow colour with 0·1 milligram nitrous acid in a litre, or else a combination of sulphanilic acid and α-naphthylamine (reagent of Griess). I have shown (Zeitschr. f. angew. Chem. 1889, p. 666) that it is best to mix both substances, dissolved in dilute acetic acid, at once, and to keep this solution ready for use; any nitrous acid getting in from the laboratory air is thus betrayed from the outset by the reagent turning pink. This colour can be removed by shaking up with zinc dust and filtering. For actual use, the solution to be tested for nitrous acid is heated up to about 80° C., and a few c.c. of the mixed reagent added to it, when a rose-colour will be developed with less than $\frac{1}{1000}$ mgr. N_2O_3 in one or two minutes. Solutions containing too much nitrous acid give only a yellow colour. In order to obtain a reagent which is not discoloured on keeping, a little of the α-naphthylamine is boiled with a few c.c. of water, the hot solution is poured off, and only this is used, mixing it with dilute acetic acid and a dilute solution of sulphanilic acid.

If any nitrous acid present is carefully destroyed by treatment with urea, the ordinary reagents, like diphenylamine, ferrous sulphate, and indigo, will indicate any nitric acid present, this not being acted upon by urea.

Selenium can be detected by the red colour imparted to a solution of ferrous sulphate, which after some little time turns into a red precipitate (not vanishing on heating like the brown colour produced by nitric oxide), or by means of sulphur dioxide. According to Jouve (Chem. Centralbl. 1901, i. p. 1389) codein or morphine prove the presence of selenium, but only when 0·5 per cent. is present, SO_2 when merely 0·01 per cent.; all of these act only on selenious, not upon selenic acid. Both acids, however, are proved by the red colour produced by the action of acetylene, if 0·001 per cent. Se is present. A little HCl hastens the separation of Se, which dissolves in the hot sulphuric acid with green colour.

Orlow (Chem. Centralbl. 1901, i. p. 480) also rejects codein and prefers SO_2, especially on heating. 5 parts H_2SO_4+10 parts water + 10 parts SO_2 solution give a red precipitate at once with 0·3 per cent. $H_2Se_2O_3$, but also with 0·03 per cent. after standing a few days or heating a few hours. Even 0·003 per cent. gives a rose-colour. Rosenheim (ibid. 1901, ii. p. 234) discusses at length the influence of selenium on the ordinary tests for arsenic.

The quantitative estimation of the impurities contained in sulphuric acid is best carried out with various portions of the sample. Usually only the following are looked for. *Lead* is estimated by diluting the acids, if concentrated, with its own volume of water and twice the volume of absolute alcohol, when all of it is precipitated by $PbSO_4$. *Iron* is estimated by reducing with pure zinc and titrating with potassium permanganate; not leaving out of sight its action upon SO_2, N_2O_3, &c. A very convenient colorimetric method for estimating traces of iron has been described by me in Zsch. f. angew. Ch. 1896, p. 3; comp. also my 'Chem. techn. Untersuchungsmethoden,' i. p. 325. *Arsenic* is estimated by reducing any arsenic acid to arsenious acid by a stream of SO_2, expelling this by CO_2, and precipitating by H_2S. The presence of lead, antimony, copper, platinum, &c. makes this process very complicated (comp. thereon McCay, Amer. Chem. Journ. vii. no. 6). If the quantity of As is somewhat considerable, it can be reduced to As_2O_3 by SO_2, followed by CO_2; the liquid is then neutralized by soda, and the As_2O_3 titrated by iodine solution (Kisling, Chem. Ind. 1886, p. 137). Further particulars are given in my 'Untersuchungsmethoden,' i. p. 327.

The *volatile impurities* of sulphuric acid are estimated as follows:—

Sulphurous acid, if at all present in weighable quantities, can be estimated by a solution of iodine according to Bunsen's method. The *acids of nitrogen* (nitrous, hyponitric, and nitric) cannot easily be present along with sulphurous acid in sensible quantity; their quantity is very considerable, however, in certain intermediate manufacturing products ("nitrous vitriol"); and the methods for estimating it are therefore of great importance. Also in chamber-acid and in more concentrated products there is much oftener nitrous or even nitric acid present than sulphurous acid; and in this case the estimation of even minute quantities is sometimes of importance, because they exert a very injurious action during the concentration of the acid in platinum.

Nitric oxide, as shown on p. 212, is soluble in sulphuric acid only in extremely slight quantities, inappreciable in any ordinary mode of testing. In practice accordingly no account need be taken of nitric oxide, especially in the case of the stronger acids, since in any case it cannot be present in sufficient quantity for estimation; and the latter need only refer to the proper acids of nitrogen. Of these, again, only nitric and nitrous acid need be taken into account. Nitrogen peroxide, N_2O_4 (formerly called hyponitric acid), when dissolved in sulphuric acid behaves exactly like a mixture of equal molecules of nitric and nitrous acid (p. 223). Nitrous acid itself does not exist in any but rather dilute sulphuric acid; in somewhat concentrated acid it exists as nitroso-sulphonic acid, $SO_2(OH)(ONO)$ (comp. pp. 215 *et seq.*). The solution of this compound in sulphuric acid behaves, however, towards oxidizing agents and in most other respects exactly like a solution of nitrous acid, which, in fact, is formed from it by dilution with water. Ordinarily in doing this, part of the NO_2H is decomposed into NO and NO_3H (p. 219), but this decomposition, which would interfere with the analysis, can be prevented by proper precautions, as we shall see later on.

First of all we must describe the methods for estimating *the total nitrogen acid,* that is *nitrous and nitric acids together,* in which case the result can be calculated as N_2O_3, N_2O_5, NO_3H, &c. Frequently, for technical purposes, the N is calculated as NO_3Na.

Of the many methods proposed for this end I only mention those which are employed for technical purposes.

The method of *Pelouze*, modified by Fresenius and others, is only adapted for the estimation of nitric acid; it is, however, sometimes used for estimating a mixture of this and of nitrous acid, after the latter has been converted into nitric acid, for instance, by chlorine, potassium bichromate, permanganate, &c. It is founded upon the fact that free nitric acid oxidizes ferrous chloride or sulphate, according to the equation

$$6\,FeCl_2 + 2\,NO_3H + 6\,HCl = 6\,FeCl_3 + 2\,NO + 4\,H_2O.$$

By means of potassium permanganate the ferrous salt, not oxidized by nitric acid, is estimated, and the quantity of the latter is calculated from that of the ferrous salt consumed.

This method is described in great detail in our first edition, vol. i. pp. 54 to 58, and second edition, vol. i. pp. 173 to 176; it is not repeated here, as the much handier nitrometer method has made it obsolete.

Another class of methods based upon the action of ferrous salts on the nitrogen acids is that first proposed by Schloesing, and subsequently modified by many others. In this class of methods, the process is carried on in such manner that all nitrous and nitric acid present is converted into nitric oxide, NO, which is then estimated in various ways—mostly by measuring its volume as a gas. This method is very much used by agricultural chemists, especially in the modification introduced by Grandeau. A table for reducing the volumes of NO to weights of N_2O_5 for various temperatures and pressures has been calculated by Baumann (Zeitschr. f. angew. Chem. 1888, p. 662; reprinted in Journ. Soc. Chem. Ind. 1889, p. 135). For nitrous vitriol this method is seldom used, because it is far more troublesome than the nitrometric methods to be subsequently described.

Many methods are based on the reduction of the nitrogen acids to ammonia by means of zinc, iron, or a combination of both. All the older forms of these methods have been superseded by the modification introduced by Ulsch (Zsch. angew. Ch. 1891, p. 241; Lunge's 'Untersuchungsmethoden,' i. p. 275), which is extensively used for the estimation of nitrate of soda, but seldom for the nitrogen acids present in sulphuric acid.

The process which is now mostly used for *the estimation of the total nitrogen acids* in sulphuric acids (as well as for that of nitrate of soda, comp. p. 96, of nitro-glycerin, and for many analogous purposes) is the *nitrometer* method, founded upon a reaction discovered by Walter Crum (Phil. Mag. 1840, xxx. p. 426). It consists in agitating the substance in question with mercury in presence of a large quantity of sulphuric acid, by which means all the nitrogen acids are converted into nitric oxide, NO, whose volume is ascertained by gasometric methods. Crum's process had been occasionally employed for the estimation of nitrates, *e.g.*, by Frankland and Armstrong; and had been specially recommended for nitrous vitriol by G. E. Davis (Chem. News, xxxvii. p. 45). But it attracted very little attention, least of all with technical chemists, because it was cumbersome and expensive (requiring a mercury trough) and withal gave no very trustworthy results, owing to the difficulty of manipulation. I drew fresh attention to this process (Berl. Ber. xi. p. 436), and made it generally accessible, both by proving its accuracy under the circumstances here mentioned, and by devising for it a special instrument, which made its manipulation extremely easy and simple. This instrument, which has since found a great variety of applications in gasometric and gas-volumetric analyses, some of which are mentioned in other parts of this work, has been called the "*Nitrometer.*" It is made in various shapes for various purposes; the shape which is used in testing nitrous vitriol is shown in fig. 44.*

Its principal portion is a glass tube, *a*, of a little over 50 cub. centims. capacity, divided into tenths of a cub. centim. At the bottom it tapers to fit an elastic joint; at the top it ends in a funnel *c* communicating with the inner part of the tube by a three-way tap. Its plug has one bore, through which the measuring-tube communicates with the funnel, and another bore through which the contents of the funnel can be run off. The division of the measuring-tube, *a*, begins from the tap itself, and goes from the top downwards. The tube *a* hangs in a clamp *e*, which can be instantaneously opened by a spring, so that the tube can be taken out. Another clamp *f*, sliding on the same stand, carries a plain cylindrical glass tube, *b*, tapering below, of the same contents and about the same diameter as the measuring-tube. The lower ends of the two tubes are connected by a thick elastic tube. *b* slides up and down in its clamp with friction. In order to use the

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* Since I first published my above-quoted paper, Campbell, Davis, Dupont, and others have made known apparatus very similar to mine, for which they have adopted my name, "Nitrometer." Not one of these, however, combines all the advantages found in the instrument constructed by me.

apparatus, *b* is placed so that its lower end is rather higher than the tap *d*, and, the latter being opened, mercury is poured in through *b* till it just comes up to the funnel *c*. As it flows into *a* from below, it will not allow any air-bubbles to remain in the tube. The tap *d* is now closed; *b* is lowered; and the acid

Fig. 44.

to be tested is run into the funnel *c* by means of a fine pipette. Of course it is necessary to have an idea of the maximum quantity of NO which may be given off without expelling the mercury from the tube altogether, and the quantity of sulphuric acid must be taken accordingly. By carefully opening the tap *d*, the acid is run into *a* without any air being allowed to enter; in a similar way the funnel *c* is washed out twice by means of pure concentrated sulphuric acid. It is not advisable to put more than 8 to 10 cub. centim. of acid into the apparatus; much better only 4 to 5 cub. centim. altogether are used; but in any case there must be an excess of strong sulphuric acid present. Now the tube *a* is taken out of the spring clamp and well shaken up. The evolution of gas in the case of nitrous acid commences at once—the acid taking a purple colour, in the case of nitric acid, after a minute or so. The reaction is ended by violent shaking for one or two minutes. Sometimes it takes a long while before the acid clears and the froth subsides, but generally this is effected in a very short time; anyhow it is necessary to wait a little, so that the apparatus may assume the temperature of the air. Now by sliding *b* up or down, the level of the mercury in this tube is so placed that it is as much higher than that of *a* as corresponds to the vitriol; say, for each 7 millim. of acid 1 millim. of mercury; or else the level of the mercury is made the same in both tubes, and the height of mercury corresponding to the layer of vitriol in the tube is deducted from the barometrical pressure. In the former case, it is easy to ascertain after reading off whether the proper compensation for the height of the acid column has been made or not. It is only necessary to cautiously open the tap *d*, over which a drop of acid has been left standing. If this is sucked in, and the level of the acid falls, there has been too little pressure, and *vice versâ*. The volume of the nitric oxide can be read off to $\frac{1}{20}$ cub. centim.; it is reduced to 0° and 760 millim. mercurial pressure, and the percentage of the acid calculated from it. Each cub. centim. of NO, measured at 0° and 760 millim., corresponds to 1·343 milligr. NO, or 1·701 milligr. N_2O_3, or 2·417 milligr. N_2O_5, or 4·521 milligr. NO_3K, or 3·805 milligr. NO_3Na. By this process, of course, nitric and nitrous acids cannot be distinguished, but are always estimated together.

After reading off, *b* is again placed higher, the tap *d* is opened so that tube *a* communicates with the small outlet tube, and thus first the nitric oxide and then the sulphuric acid, muddy with mercuric sulphate, is driven out. When the mercury begins to run out as well, the tap is closed, and everything is again ready for a new testing. If any sensible quantities of sulphurous acid be present (as proved by the smell), it is best to add a very little powdered potassium permanganate to the sulphuric acid, avoiding any considerable excess.

The nitrometer was first provided with a three-way tap on Cl. Winkler's principle, with one transverse and one longitudinal bore; but now another arrangement, known as the "Greiner-Friedrichs" or the "Geissler-Miescher" tap, and shown in the diagram, is preferred, which admits of much easier manipulation and is far less liable to leakage.

It has been stated by T. Bayley that it is necessary to dilute the acid contained in the nitrometer at the close of the experiment, in order to expel the nitric oxide dissolved by the sulphuric acid, otherwise an error of about 0·5 c.c. is committed. I have proved this to be wrong, no measurable quantity of NO being dissolved by the acid contained in the nitrometer (Journ. Soc. Chem. Ind. 1885, p. 447, and 1886, p. 82). This could not be contradicted by Mr. Bayley, who, however, contended that the iron contained in the acid as ferrous sulphate acted as solvent for NO. I replied to this (Chem. News, 1886, liii. p. 289) that the quantity of iron found in any commercial acid would never lead to any appreciable error of this kind, more particularly as it would be present as ferric sulphate.

From the volume of NO read off, and reduced to 0° C. and 760 mm., the nitrogen compounds present are calculated by the following table (p. 259), in which column *a* gives milligrams, and *b* per cent. by weight, when employing in the nitrometer 1 c.c. acid of 140° Tw.

In spite of the very great convenience, speed, and accuracy of the nitrometric estimation of the nitrogen acids, many chemists might have abstained from using it because the unavoidable reduction of the volume of NO to 0° C. and 760 millim. pressure appeared too tedious to them. In order to overcome this objection, I have calculated tables which admit of reducing any volume of gas from 1 to 100 from any given temperature to 0° C., and from any given pressure to 760 millim., by simple reading off. These tables were given in the Appendix to my first edition; they

c.c. NO.	N.		NO.		N_2O_3.		NO_3H.		NO_3Na.	
	a.	*b.*	*a.*	*b.*	*a.*	*b.*	*a.*	*b.*	*a.*	*b.*
1.	0·627	0·0366	1·343	0·0785	1·701	0·0995	2·820	0·1648	3·805	0·2225
2.	1·254	0·0732	2·686	0·1570	3·402	0·1990	5·640	0·3296	7·610	0·4450
3.	1·881	0·1098	4·029	0·2355	5·103	0·2985	8·460	0·4944	11·415	0·6675
4.	2·508	0·1464	5·372	0·3140	6·804	0·3980	11·280	0·6592	15·220	0·8900
5.	3·135	0·1830	6·715	0·3925	8·506	0·4975	14·100	0·8240	19·025	1·1125
6.	3·762	0·2196	8·058	0·4710	10·206	0·5970	16·920	0·9888	22·830	1·3350
7.	4·389	0·2562	9·401	0·5495	11·907	0·6965	19·740	1·1536	26·635	1·5575
8.	5·016	0·2928	10·744	0·6280	13·608	0·7960	22·560	1·3184	30·440	1·7800
9.	5·643	0·3294	12·087	0·7065	15·309	0·8955	25·380	1·4832	34·245	2·0025

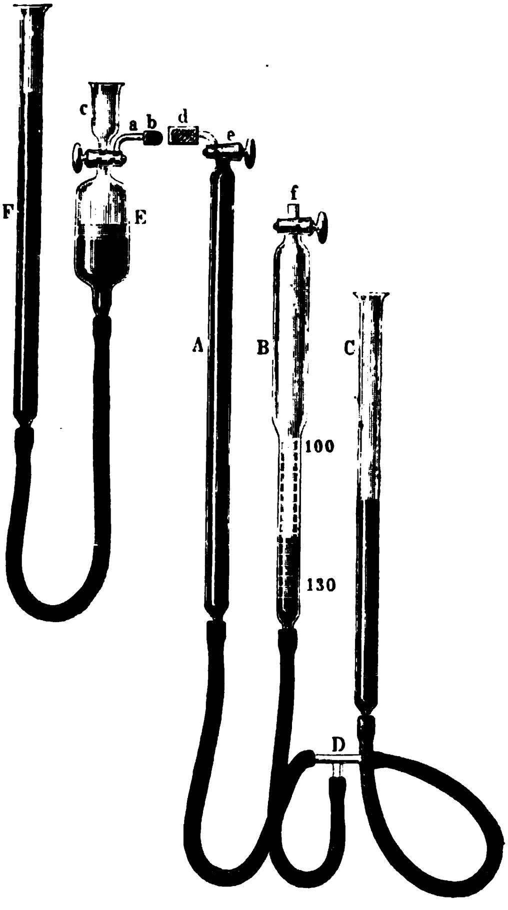
are also contained in Lunge and Hurter's 'Alkali-Maker's Pocket-book,' and are also separately published for use as wall-tables by F. Vieweg & Sohn, Brunswick. Other tables, requiring very little more time for use, are found in Winkler-Lunge's 'Handbook of Gas-Analysis,' 2nd edition, pp. 177 *et seq.*

I abstain here from giving these or any other tables, as an instrument invented by myself, and called the "gas-volumeter" (Zeitschr. f. angew. Chem. 1890, p. 139; Berliner Berichte, 1890, p. 440), has made unnecessary all calculations and tables in connection with the reduction of volumes of gases to 0° and 760 millim. This instrument, as shown in fig. 45 (p. 260), consists of three glass tubes, all joined by very strong elastic tubes to a three-way pipe D, and sliding upwards or downwards in strong clips. Tube A is the measuring-tube, B the reduction-tube, C the level-tube. A is divided into tenths of cub. centim. and generally holds 50 c.c.; where larger volumes of gases are to be measured it is shaped like B, and holds 60 or 100 c.c. in the upper, wider portion, and another 40 c.c. (divided into $\frac{1}{10}$ c.c.) in the lower, narrower portion. The "reduction-tube" B holds 100 c.c. in the upper part, and another 30 c.c. (divided into $\frac{1}{10}$ c.c.) in the lower part. This tube is set once for all in the following way:—After putting the apparatus together and partly filling it with mercury, the temperature close to B and the barometric pressure are taken, and it is calculated, by the well-known formula

$$\frac{(273+t)760}{273\times b}$$

(where *t* denotes the temperature in 0° C., *b* the height of the barometer in millimetres), what would be the volume of 100 c.c. dry air under the then atmospheric conditions. (This calculation can be abridged by using any of the above-mentioned tables, if they are at hand.) Suppose *t*=20°, *b*=750 millim. In this case 100 c.c. of dry air would occupy the volume 108·8 c.c. We now move B and C so that, tap *f* being open, the level of the mercury in B is at 108·8, whilst the mercury in C is, of course, at the same level. Previously to this we have introduced a drop of strong sulphuric acid into B, but not sufficient to reach over the meniscus of the quicksilver, which would be an impediment to taking the readings; this is done, because gases have afterwards to be measured in the *dry* state.

Fig. 45.



(In the more frequent case in which this instrument is employed for measuring *moist* gases, in lieu of sulphuric acid, a drop of water is introduced into B, and the calculation is made by deducting from the barometric pressure the tension of aqueous vapour corresponding to the existing temperature.) Now tap *f* is closed, and is secured so that no air can enter or escape through it. In lieu of this tap a capillary tube may be provided which is sealed by a small flame, after having put a perforated piece of asbestos cardboard over the top of tube B, to prevent its temperature rising during the sealing-operation. The best way of closing tube B is by means of a mercury-scaled tap as described by me in Berl. Ber. 1892, p. 3158.

It is quite evident that every time the level-tube C is raised so that the mercury in B rises to the point 100, the air within B is compressed to the volume it would occupy at 0° and 760 millim. independent of the temperature and barometric pressure actually existing. Now suppose we have evolved or carried over into tube A a certain volume of gas, and we adjust the position of the three tubes so that the mercury in B stands at 100°, and that in A exactly at the same level, it is evident that the gas in A is under the same pressure as in B; and, supposing its temperature to be the same (which will be the case if the two tubes are close together), the gas in A will be equally compressed as that in B to the volume it would occupy at 0° and 760 millim. barometric pressure. The reading taken in A thus yields at once the corrected volume without having to look at a thermometer or barometer, or use any calculations or tables.

Tube A might be an ordinary nitrometer; but it is far preferable to use it only as a measuring-tube, and thus to keep it always clean and dry, whilst the nitrometric operation proper is carried out in the auxiliary "agitating-vessel" E. This is a non-graduated vessel, holding 100 to 150 c.c., and connected by a strong elastic tube with the level-tube F. The vessel E bears at the top the usual three-way tap and cup *c*. The side-tube *a* can be closed by a small ground-on cap *b*, or else by an india-rubber cap. Before commencing the analytical operation, the tube F is raised so that the mercury just issues out of *a*; cap *b* is now put on and tap *c* is closed. Now the nitrous vitriol (or solution of nitrate of soda, comp. p. 96) is introduced through *c*, by carefully lowering F, so that only the liquid, but no air, enters into E; strong sulphuric acid follows, to rinse out cup *c*; the tap is now entirely closed, and E is violently shaken till the decomposition is complete and no more NO is given off. The cap *b* prevents the mercury in tube *a* from being thrown out in the shaking. The instrument is allowed to cool down, and is then put in the position shown in the diagram, so that the small tubes *a* and *d* are on the same level. Previously a short piece of india-rubber tube has been slipped over *d*, and by raising C the mercury has been forced right to the end of *d*. Now cap *b* is taken off, and *a* is introduced into the short elastic tube, till the glass tubes *a* and *d* touch. Now tube C is lowered and F raised (as shown in the diagram), and tap *c* is cautiously opened (*e* having been left open before). The gas will thus be transferred from E into A; at the moment when the sulphuric acid has entered into the bore of *e*, but before it has got inside of A, tap *e* is closed. Now the reading is taken as described above; the apparatus EF may be detached at any time and cleaned as occasion requires.

The readings of the volume of NO taken in tube A may be converted into grams of N_2O_3 or $NaNO_3$, &c., by means of the table given on p. 259. If nitrate of soda has to be analyzed, each c.c. will indicate 3·805 milligr. $NaNO_3$; hence, if 0·3805 gram of nitrate were employed for the test, the number of c.c. of NO would at once indicate the percentage of $NaNO_3$. In the case of nitrous vitriol the quantity will usually not be weighed, but measured by means of a pipette, and the results obtained must then be divided by the specific gravity of the acid to reduce them to weight percentage. If the acid is near 140° Tw., this is unnecessary; for in this case a 1 c.c. pipette will deliver 1·70 gram acid, and as each c.c. of NO indicates 0·0017 N_2O_3, this means that the number of c.c. read off is exactly = tenths of a per cent. of N_2O_3 by weight of the nitrous vitriol.

We now proceed to the estimation of *nitrous acid*, or, more properly speaking, of *nitrososulphuric acid*, present in sulphuric acid, which is mostly sufficient for testing the "nitrous vitriol" from the Guy-Lussac tower.

Among all the analytical methods founded upon the oxidation of nitrous acid, both the most convenient and the most accurate is that with *potassium permanganate*, first proposed by Feldhaus. Even for scientific purposes there is not a more accurate method for estimating nitrous acid in an acid solution than this, if other oxidizable bodies be absent.

Even nitric oxide is oxidized by this reagent, according to this equation:

$$10\,NO + 6\,MnO_4K + 9\,SO_4H_2 = 10\,NO_3H + 3\,SO_4K_2 + 6\,SO_4Mn + 4\,H_2O.$$

Accordingly the seminormal solution of permanganate, each cub. centim. of which corresponds to 0·004 O, will show 0·005 NO for each cub. centim. Thus, on the one hand, nitric oxide can be estimated quantitatively by this reagent: on the other hand, the nitric oxide would make the estimation of nitrous acid inaccurate if it were present at the same time, which, fortunately, is not the case in sulphuric acid to an appreciable extent.

Nitrous acid itself is oxidized by permanganate, according to the equation:

$$5\,N_2O_3 + 4\,MnO_4K + 6SO_4H_2 = 10\,NO_3H + 2\,SO_4K_2 + 4\,SO_4Mn + H_2O.$$

Here every cub. centim. of seminormal permanganate solution corresponds to 0·0095 gram N_2O_3.

The process formerly in use, where the permanganate solution was run into the nitrous vitriol, has been shown to be quite inaccurate by my investigations (owing to the formation of NO and HNO_3) and has been replaced by the plan proposed by myself, namely, manipulating in the following way:—The permanganate is not run into the acid, but, on the contrary, a certain volume of permanganate solution is taken, and the nitrous vitriol is run in from a burette slowly, and with constant shaking, till the liquid is just decolorized. In the cold there is some loss of time, since the very dilute solution of permanganate is no longer acted upon instantaneously. This loss of time can be avoided by working at 30° to 40° C., but *no higher*. When working with concentrated sulphuric acid, this temperature is attained without any special means; otherwise the permanganate solution is heated up beforehand. If seminormal solution is employed, it is diluted with about 100 c.c. of tepid water. Sometimes a brown precipitate (of hydrated manganese peroxide) is formed in the operation; but this dissolves later on, and the final result is quite as correct in these as in any other cases.

In testing chamber acid, at most 5 c.c. of seminormal permanganate should be employed; otherwise the quantity of sulphuric acid required for decolorizing it will be inconveniently large. For proper "nitrous vitriol" from the Gay-Lussac tower up to 50 c.c. permanganate may be taken. If the number of c.c. of permanganate is called x, and that of the acid required for decolorizing it y, the quantity of N_2O_3 present in grams per litre of acid is $\frac{9 \cdot 5\, x}{y}$, calculated as

$$NO_3H = \frac{15 \cdot 75\, x}{y},$$

or as

$$NaNO_3 = \frac{21 \cdot 25\, x}{y}.$$

The following table saves the calculation in all cases in which $x = 50$. The column y gives the number of cub. centim. of nitrous vitriol used, a the percentage in grams per litre, and b the percentage by weight for acid of 140° Tw. (For other strengths the percentage by weight is calculated by dividing the figures of column a by 10 times the specific gravity.) The figures in column a also indicate 0·01 lb. avoirdupois per gallon, or, as nearly as possible, ounces per cubic foot.

Table for testing Nitrous Vitriol.

Acid consumed.	N_2O_3.		NO_3H.		NO_3Na.	
y. c.c.	a. grms. per litre.	b. per cent.	a. grms. per litre.	b. per cent.	a. grms. per litre.	b. per cent.
10	47·5	2·80	78·8	4·62	106·2	6·22
11	43·2	2·54	71·6	4·20	96·5	5·65
12	39·6	2·33	65·7	3·85	88·5	5·18
13	36·5	2·15	60·6	3·55	81·7	4·78
14	34·0	2·00	56·2	3·28	75·9	4·44
15	31·7	1·86	52·5	3·07	70·8	4·14
16	29·5	1·74	49·3	2·89	66·4	3·91
17	27·9	1·64	46·3	2·71	62·5	3·65
18	26·4	1·55	43·7	2·56	59·0	3·45
19	25·0	1·47	41·5	2·43	55·9	3·27
20	23·7	1·38	39·3	2·30	53·1	3·11
21	22·6	1·33	37·5	2·19	50·6	2·96
22	21·6	1·27	35·7	2·09	48·3	2·82
23	20·6	1·21	34·2	2·00	46·3	2·71
24	19·8	1·17	32·8	1·92	44·4	2·60
25	19·0	1·12	31·5	1·84	42·5	2·49
26	18·3	1·08	30·3	1·77	40·8	2·39
27	17·6	1·03	29·1	1·71	39·4	2·30
28	17·0	1·00	28·1	1·64	38·0	2·22
29	16·4	0·96	27·1	1·58	36·7	2·15
30	15·8	0·93	26·3	1·54	35·5	2·08

Table for testing Nitrous Vitriol (continued).

Acid consumed.	N_2O_3.		NO_3H.		NO_3Na.	
y. c.c.	*a.* grms. per litre.	*b.* per cent.	*a.* grms. per litre.	*b.* per cent.	*a.* grms. per litre.	*b.* per cent.
31	15·3	0·90	25·5	1·49	34·3	2·01
32	14·8	0·87	24·6	1·44	33·3	1·95
33	14·4	0·85	23·9	1·40	32·3	1·89
34	13·9	0·82	23·2	1·36	31·3	1·84
35	13·6	0·80	22·5	1·32	30·4	1·78
36	13·2	0·78	21·9	1·28	29·5	1·73
37	12·8	0·75	21·3	1·25	28·7	1·68
38	12·5	0·73	20·7	1·21	28·0	1·64
39	12·2	0·72	20·2	1·18	27·3	1·60
40	11·9	0·70	19·7	1·15	26·6	1·56
41	11·6	0·68	19·2	1·12	25·9	1·52
42	11·3	0·66	18·8	1·10	25·3	1·48
43	11·0	0·65	18·3	1·07	24·7	1·45
44	10·8	0·63	17·9	1·05	24·2	1·42
45	10·6	0·62	17·5	1·02	23·6	1·38
46	10·4	0·61	17·1	1·00	23·1	1·35
47	10·1	0·59	16·8	0·98	22·6	1·32
48	9·9	0·58	16·4	0·96	22·2	1·30
49	9·7	0·57	16·1	0·97	21·7	1·27
50	9·5	0·56	15·8	0·925	21·3	1·25
55	8·6	0·50	14·4	0·835	19·3	1·13
60	7·9	0·46	13·1	0·765	17·7	0·04
65	7·3	0·43	12·1	0·705	16·4	0·96
70	6·8	0·40	11·2	0·655	15·2	0·89
75	6·3	0·37	10·5	0·615	14·15	0·827
80	5·9	0·35	9·85	0·575	13·3	0·778
85	5·6	0·33	9·2	0·538	12·5	0·730
90	5·3	0·31	8·7	0·510	11·8	0·692
95	5·0	0·29	8·3	0·485	11·2	0·655
100	4·7	0·28	7·9	0·462	10·6	0·620

In the presence of *other oxidizable substances*, such as sulphurous acid, ferrous salts, organic substances, &c., all oxidation methods are of course inexact—whether the bleaching-powder, or the bichromate, or the permanganate process. Generally those impurities are too insignificant to do any harm; but, especially where large quantities of nitrous acid are present, as in the nitrous vitriol from the Gay-Lussac towers, the permanganate process is quite sufficient for the purpose of checking the course of manufacture. Of the oxidizable substances only arsenious acid sometimes occurs in sufficient quantities to affect the results sensibly, but to a small extent only, in nitrous vitriol, where it is mostly changed into arsenic acid.

The estimation of nitrous acid by means of aniline, which is converted into a diazobenzol salt, the end of the reaction being shown by potassium iodide and starch, has been practised for some time at several colour-works, long before it was published by Green and Rideal (J. Soc. Chem. Ind. 1886, p. 633). According to comparative tests made in my laboratory, it offers no advantage whatever over the very much less troublesome permanganate method, and may lead to serious errors (Zsch. angew. Ch. 1891, p. 629, 1902, p. 169).

Minute quantities of nitrogen acids cannot be quantitatively estimated by the above methods, but the *colorimetric estimation of slight quantities of nitrous acid,* as I have shown in Zsch. f. angew. Ch. 1894, p. 348, can be performed by Griess's reagent, modified as follows :—0·1 gram white α-naphthylamine is dissolved by boiling in 100 c.c. water for a quarter of an hour; then 5 c.c. glacial acetic acid (or its equivalent in ordinary acetic acid) and a solution of 1 gram sulphanilic acid in 100 c.c. water are added. The solution is kept in a well-stoppered bottle; if it turns pink it is decolorized by shaking with zinc-dust and filtering. A very slight colour does not interfere with its use, as only 1 c.c. is employed for 50 c.c. of the solution to be tested. 1 c.c. of the reagent indicates $\frac{1}{1000}$ milligram nitrous nitrogen in 100 c.c. water by turning the water pink in 10 minutes. Strong mineral acids retard or stop the reaction, but this can be remedied by adding a large excess of pure sodium acetate.

For quantitative use a standard solution is prepared as follows :—0·0493 gram pure sodium nitrite, containing 0·010 gram nitrogen, is dissolved in 100 c.c. water, and 10 c.c. of this solution is drop by drop added to 90 c.c. pure sulphuric acid; the resulting mixture contains $\frac{1}{100}$ milligram of nitrous nitrogen in a perfectly stable form. Two colorimeter cylinders are charged as follows :—Each of them receives 1 c.c. of the Griess-Lunge reagent, 40 c.c. of water, and about 5 grams of solid sodium acetate. To one of these is added 1 c.c. of the standard solution, to the other 1 c.c. of the acid to be tested. The contents of each cylinder are at once thoroughly mixed, and after 5 or 10 minutes the colours are compared. If they do not correspond, the more strongly coloured liquid is diluted up to the point where layers of equal thickness show the same depth of colour in both solutions, and the percentage of nitrous nitrogen is calculated from the amount of dilution.

Very minute quantities of *nitric acid* are best estimated by the *colorimetric brucine process,* described by me, Zsch. angew. Ch. 1894, p. 347, the principle of which consists of comparing the yellow colour obtained by heating to about 70° with brucine with a standard solution of nitric acid. As a rule, nitric acid is not estimated by itself in sulphuric acid, but indirectly, by estimating the total nitrogen acids by means of the nitrometer (p. 253) and deducting the nitrous acid found by the permanganate method (p. 262).

CHAPTER IV.

THE PRODUCTION OF SULPHUR DIOXIDE.

A. BRIMSTONE-BURNERS.

ALREADY in the historical part attention has been drawn to the point that important progress was made in the manufacture of sulphuric acid when the periodical combustion of sulphur within the acid-chambers was replaced by continuous work in special apparatus attached to the chambers. This led to making the sulphur-burners altogether independent of the chambers, and conveying the gas generated in the former by a flue into the latter.

Whilst in the old periodical style of working only the oxygen actually present in the chamber could come into play, and therefore after every combustion the chamber had to be supplied with fresh air by opening the door and a special valve, of course at the expense of much inconvenience and loss of gas, in the continuous method of work the necessary air constantly enters the burner by suitable openings at the same rate as the products of combustion are aspirated into the chamber by the draught prevailing throughout the apparatus. The continuity of work must be further aided by employing a combination of several burners, so that there shall always be burning sulphur present. There are also burners to which the brimstone is continuously supplied, in order to avoid the drawback of irregular supply of air and gas occurring even with the combination of several ordinary burners.

The plainest sulphur-burners, such as were the most usual in England, are represented in figs. 46 to 48. The burner consists of a brick chamber covered by an arch, the bottom being formed by a cast-iron plate, *a*, separately shown in fig. 48. This plate at the two long sides and one of the ends has a somewhat slanting-up flange of 3 inches height—in front, however, only 1 inch, so as to get out the ashes more easily. The plate does not go right through the burner, but leaves the last third of it free; in this part of the chamber the sulphur vapour, which is always formed, can mix with the excess of air and be burned. Rarely, however, is this completely performed, and there is generally some sulphur carried away unburned. This not only causes a loss, but also easily leads to the chamber-acid getting muddy and being covered with a thin film of sublimed sulphur, which prevents the contact between the bottom acid and the gas, very necessary for the chamber process. The burner is further provided with an

Fig. 46.

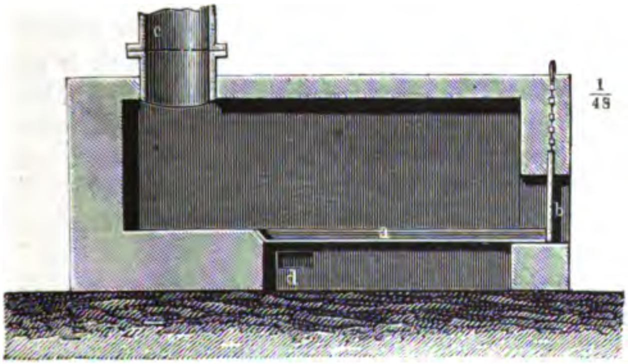


Fig. 47.

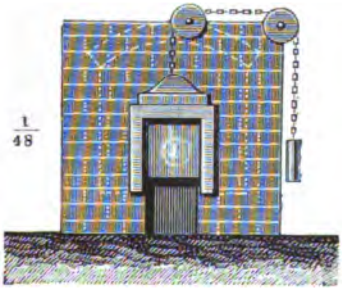
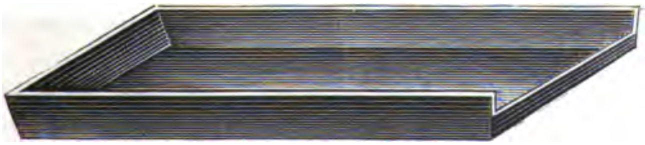


Fig. 48.



iron door, *b*, sliding in a frame and adjustable by a chain and balance-weight; also with a pipe, *c*, for taking away the gas. An air-channel, *d*, below the plate is in connection with a small chimney, or sometimes only with the open air, in order to cool the metal plate to some extent and prevent the sublimation of sulphur. There are always several furnaces of this kind combined together; each of them, with plates of 8 feet × 4 feet, can burn 5 cwt. of brimstone in 24 hours, which is put in in 6 portions, one every 4 hours; if four furnaces are combined, one of them is charged every hour. Sometimes, however, much larger and more frequent charges are made (see below*). In these burners, usually at the same time, the nitric acid is liberated by placing cast-iron pots, provided with three feet and containing a mixture of nitre and vitriol, amidst the burning sulphur by means of large tongs.

For a start the plates are heated by a small fire of wood shavings, the door being left open, not till the iron becomes red-hot, but only till the first charge of sulphur ignites of its own accord or can be easily lighted by a red-hot iron; the further charges always find the burner sufficiently warm. A special fire-grate below the plate, to be used only at the start, is sometimes provided, but is quite unnecessary. The admission of air is regulated by opening the door, *b*, more or less widely; and its position is fixed by putting a wedge underneath it, or by hooking the balance-chain to a nail driven into the brickwork outside. At the commencement, when the chambers are filled with air, the damper in the draught-tube is only opened gradually, to drive away the air more thoroughly.

The style of working is generally rather rough; it must be mentioned that such burners are nowadays seldom found in large works, where more supervision can be used. Before the attendant pulls up the door, he convinces himself regarding the state of the chambers so as to judge how much nitre he is to "pot" along with the brimstone. Often the nitre is merely measured by guesswork. First the brimstone is thrown in; the door is immediately let down, then a sufficient quantity of chamber-acid is poured into the nitre-pots, always by guesswork; the door is opened again, and the pots are placed in the brimstone, now already on

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* Davis (Chemical Engineering, ii. p. 123) states that up to 2 lb. of brimstone can be burned per square foot per hour. This is more than the maximum I have ever found in practice. It is best not to reckon upon much more than 1 lb. per square foot per hour.

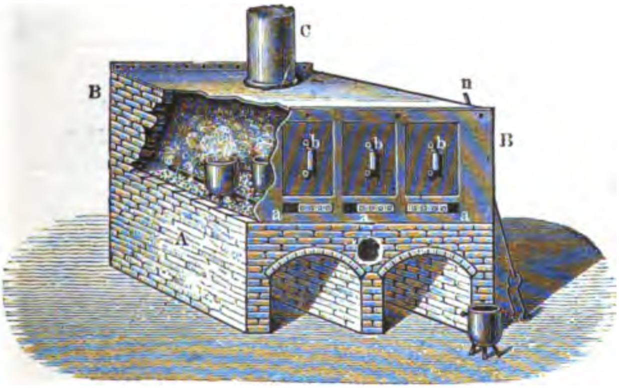
fire, by means of an iron fork made for the purpose. The heat produced by the progress of the combustion drives off the nitric acid, and this enters the chambers along with the sulphur dioxide.

When the time is up, the door is raised again, and the ashes are raked out; first, however, the nitre-pots are lifted out and emptied of their liquid contents. Then a new charge is made as above, and so forth. In all other sulphur-burners, excepting the continuous ones, the work is carried on in the same manner: only the introduction of the nitre sometimes takes place in a less rough way, or nitric acid is used directly in the chambers.

It is a sign that the burner is working well if the brimstone burns with a pure blue flame; as soon as the flame takes a brown tinge, it indicates that much sulphur is subliming, and care must then be taken to cool the plate by the flue underneath.

A somewhat more perfect apparatus is shown in fig. 49. A is the foundation, B the chamber for burning the sulphur, C the gas-pipe. The foundation carries a cast-iron plate which covers the whole furnace-bottom and is inclined a little forward. The combustion-chambers are at the sides bounded by brick walls, but in front, at the back, and at the top by cast-iron plates; in front also are the charging-doors, *b b*, and small openings, *a a*, provided with slides for regulating the access of air. The furnace-bottom is divided by 3- or 4-inch iron bars into three compartments, corresponding to the doors and draught-holes, which are served by turns. Inside the pots are visible, into which the mixture of nitre and sulphuric acid is charged. The details of construction

Fig. 49.



are often very different from those shown in the diagram; there are burners with more or fewer working compartments, with different regulation of air, with rails over the bottom plates for pushing in a box instead of the nitre-pots, &c. The nitre-pots must receive a very small charge: otherwise the danger of boiling over is considerable, and the sodium sulphate among the sulphur is very troublesome. When nitric acid is used in the chambers, the nitre-pots are not required at all.

Sometimes the iron sides of the sulphur-burners are made double, and an air-channel is left in the space between. Thus, of course, the temperature of the burner can be regulated to a nicety by opening up a draught through the double iron wall when the burner gets too hot, and shutting up the draught when it gets too cold.

Fig. 50.

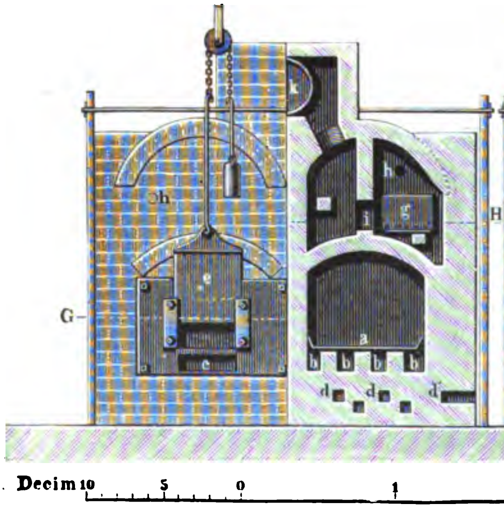


Fig. 51.

The diagrams figs. 50 to 53 show a set of two burners free from most of the drawbacks mentioned. Fig. 53 is a sectional plan taken at two different levels; fig. 52 a longitudinal section; fig. 50 half front elevation, half cross section; fig. 51 back elevation.

a is the cast-iron bottom plate for burning the sulphur; it is carried hollow on pillars; and the channels *b b* formed thereby underneath the plate communicate with the outer air by the opening *c*, so that the plate can be cooled from below. The channels, *d d*, left in the foundation a little further below, communicate with this system, and ultimately end outside *d'*. Owing to the difference of level and temperature, the air must always enter at *d'* and get out at *c*; its quantity can be easily regulated by partially closing *c*. The door *e* is hung in the usual way. The gas of the burner does not go straight to the chamber, but first ascends through the opening *f* into a space separated from the burner proper by an arch. Just above the opening there is a grating, on which the nitre-pots are put, being introduced by the door *g*.

Fig. 52.

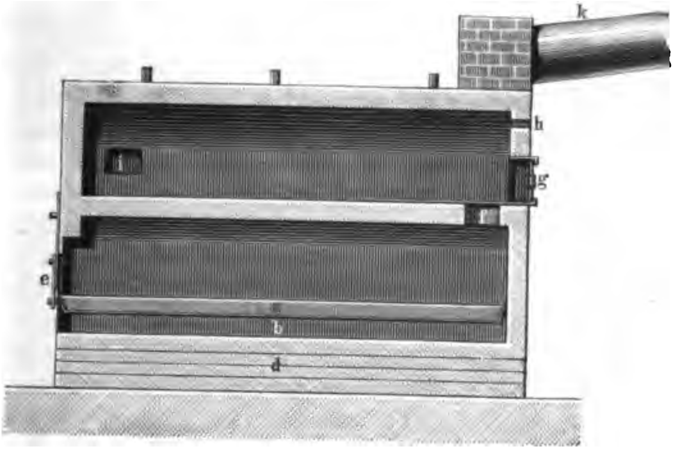
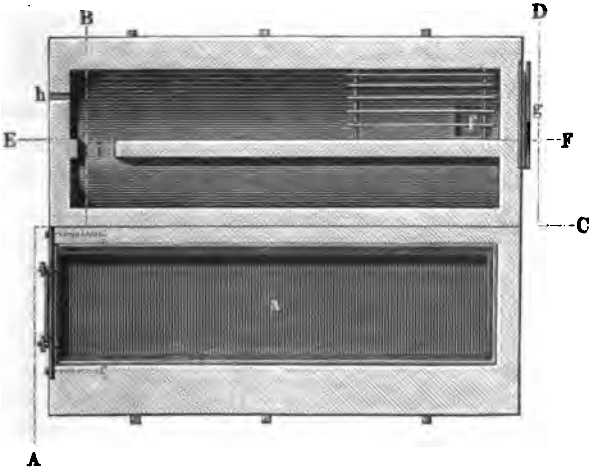


Fig. 53.



There is here a small hole *h*, lined with an iron tube, for admitting a little more air to the upper compartment and burning any sublimed sulphur. The gas first returns to the front, then back again through the hole *i* and the second half of the upper compartment, and at last escapes through the cast-iron pipe *k*, common to two burners, whose upper stories are accordingly not built alike, but are symmetrical.

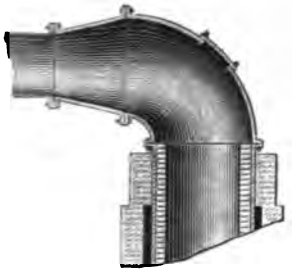
This burner (known to myself from actual use) admits of very good regulation; the sublimed sulphur on its long course through the upper story is either deposited as such or burnt, and cannot get into the chambers. The boiling-over of the nitre-pots can here be rendered harmless by simple contrivances. This burner is in some points analogous to that of Harrison Blair (see p. 277), but it is much simpler and adapted for a smaller scale of work. As a rule the working-doors are closed within a very small fraction, and the admission of air to the upper story is regulated by more or less closing the hole *b*. Four such furnaces work together; every half-hour one of them is charged with ½ cwt. of brimstone.

Fish (B. C. p. 7757, 1891) makes the burner-bed incline to one side, so that the sulphur can be gradually moved towards that side, where the ashes are raked out.

In order to escape the drawback common to all sulphur-burners, viz. the high temperature causing a sublimation of sulphur (which some have tried to avoid by wetting the brimstone with water), and even to turn it to some use, the cover of the burner is occasionally employed for drying wet materials; it has sometimes been made in the shape of a pan for heating water or for concentrating acid, which is the most rational plan.

A large brimstone-burner, covered in with evaporating-pans, is shown in figs. 54 to 56. Fig. 54 is a sectional elevation on the lines E F G H of fig. 55; fig. 55 is a plan on lines A B C D of fig. 54; fig. 56 a front view. These diagrams, representing a furnace at work in America, have been kindly supplied by Dr. Karl F. Stahl, of Johnstown (Pa.). Its bottom, roof, and sides are formed of cast-iron plates, 1 in. thick, with 6-in. flanges bolted together and caulked with rust-cement. A brick wall, 9 in. thick, is carried all round, leaving a hollow space of 2 in. from the plates; a few of the bricks near the top and bottom are put in loosely, which permits of air-cooling in very hot weather. The lead pans placed on the iron roof are 3′ 6″ × 10′ 10″ × 7″, the weight of the lead

Fig. 54.



Scale $\frac{1}{71}$.

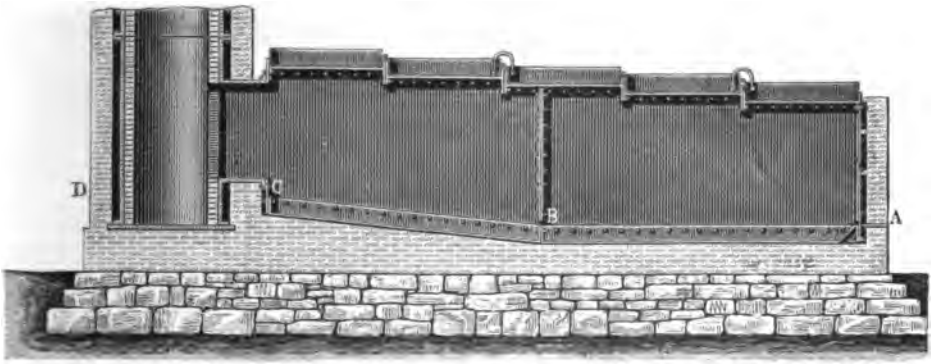
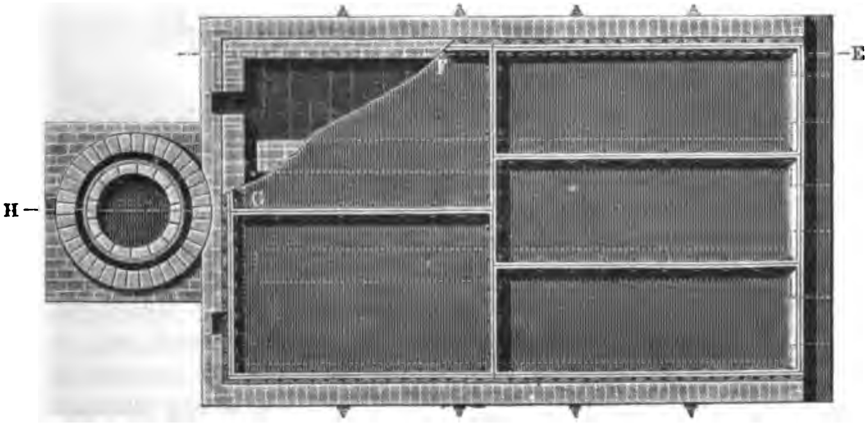


Fig. 55.

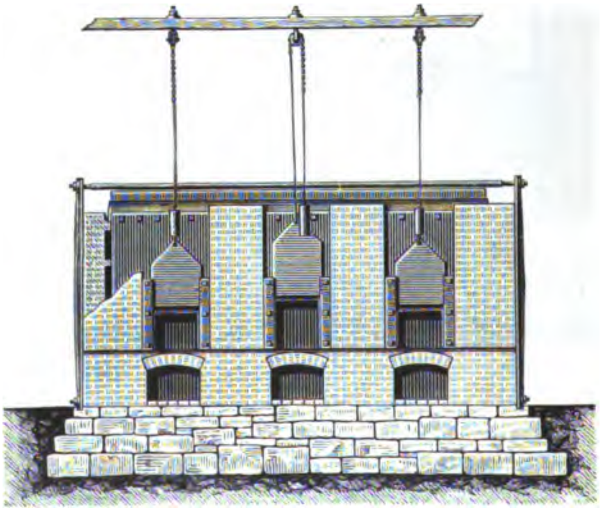


being 8 to 12 lb. per super. foot. The furnace bottom consists of five plates, as seen in fig. 55 ; on each of the three front plates (3′ 6″ × 12′) from 1000 to 1300 lb. of brimstone can be burnt in 24 hours.

An arrangement, made by Kuhlmann, for combining a steam-boiler with a sulphur-burner (1st edition of this work, pp. 139, 140), did not answer at all, and has been discontinued.

All the sulphur-burners hitherto described are built on the intermittent plan; and unless a number of them were working together, they would yield a very unequal current of gas. As the sulphur must, of course, be allowed to burn off as completely as possible, the furnace in the final stage, and especially just before being recharged, yields very little sulphur dioxide, whilst it is not possible to regulate the draught so that exactly so much less air is introduced as less sulphur is burnt. When at last the door is opened for a new charge, a very large quantity of air rushes into the burner and further on to the chambers, without any sulphur dioxide whatsoever. This irregularity, very prejudicial to the chamber process, is certainly to a great extent neutralized by the fact that always several furnaces (three, four, five, or more) work together in such a way that they are charged in turns ; for instance, with a four hours' shift and four furnaces

Fig. 56.



one furnace is charged each hour, and thus gives out least gas when its neighbours are fully burning. It has, however, been several times attempted to construct really *continuous burners*, which would save much labour, and, moreover, give a much better-regulated current of gas than can be obtained with single burners.

Two such continuous burners have been constructed by Petrie; we refer for diagrams and descriptions to our 1st edition, pp. 141 and 142.

Fig. 57.

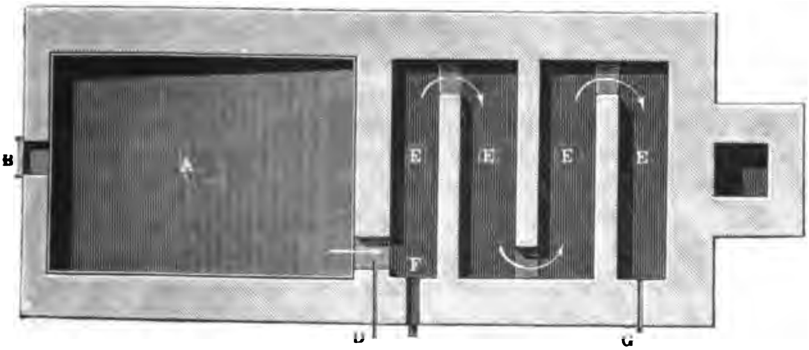
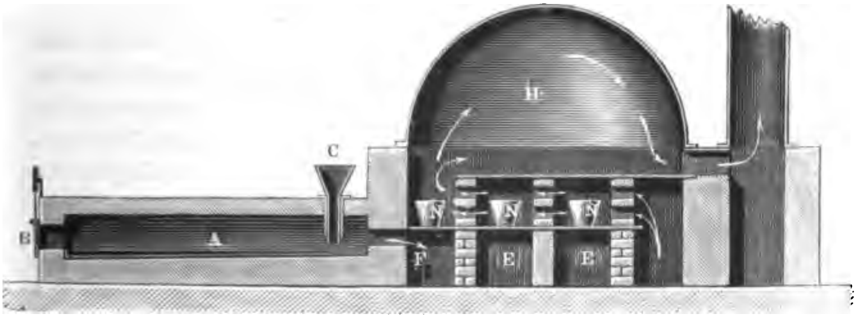


Fig. 58.



The object pursued by Petrie is attained in a more perfect way by the furnace of Harrison Blair, in which the volatilization of the sulphur, which otherwise is a source of inconvenience, is utilized to make the burning continuous. The apparatus consists of three parts, one of which serves for partly burning the sulphur and entirely volatilizing the unburnt portion; the second serves for completely burning the latter portion, the third for decomposing the nitre. Although the two former compartments are at a full red-heat during the process, sublimation of sulphur is as good as impossible; and the process is as nearly continuous as possible, since the residue need only be withdrawn once in 24 hours. Fig. 57 shows a plan, fig. 58 a sectional elevation, of this burner. A is the space corresponding to an ordinary burner-plate, which has rather high sides and a descent towards the door; but 2 feet from the door it rises again a little, so that the residue raked to that part can burn out completely before it is removed by the door B, which takes place once in 24 hours. When this has been done, the residue raked together from the other parts of the burner is brought to the same place and allowed to burn for 24 hours again. The bottom of the burner is not made of iron, but of closely-set bricks with well-grouted joints. This space A is 9 feet long, 6 feet wide, and 1 foot high. The door B is an iron plate, loosely sliding in a frame, but a little slanting so that it closes almost air-tight, and is easily removed. It is perforated by a number of holes, which can be either partly or entirely closed by a slide. The brimstone is either put in once every 24 hours through the working-door, or gradually through a funnel C. C is continued by a 7-inch cast-iron pipe to within 6 inches from the bottom of the chamber; it is surrounded by a wider pipe to protect it against being burnt too quickly. The funnel and its continuation are always filled with brimstone; and this is continually replaced as it melts off at the bottom. The simpler method of charging once every 24 hours through the door seems after all to have succeeded best. The admission of air through B is regulated so that only sufficient sulphur is burnt for keeping up the heat of the furnace; the largest part is simply evaporated. At the same time the regulation of the access of air allows of spreading the process evenly over the whole day. The walls of the furnace are made 1½ brick thick, in order to retain the heat. The mixed gas and vapours enters through an opening of 9×9 inches (which can be closed by a fire-clay damper D) into the combustion-space proper, E E, 8 × 6 feet, divided by three partitions into four compartments, communicating alternately in front and back by openings 9 inches square. Here at the same time fresh air enters by the opening F, which is provided with a damper of 3 × 8 inches. Now sufficient air is admitted for burning all the sulphur, which can be recognized with certainty by the fact that on opening the plug G the entering air does not produce a new flame. The roof of the combustion-space, E, is formed of fire-tiles, above which a second story, the nitre-oven, is situated. There are three rows of nitre-pots, N, separated by reticulated brickwork, which also serves to support another roof of fire-tiles for covering the nitre-oven, altogether 18 inches high. The diagram shows how the hot gas circulates round the nitre-pots. The pots are renewed every six hours, so that every two hours another row of pots has its turn. The hot gas, mixed with the nitre-gas, first passes underneath the cast-iron dome, H, for a partial cooling, then through an iron pipe, 24 feet high, into a small cooling-chamber 18 feet long, 5 feet wide, and 1½ foot high (whose bottom and top are covered with water), and then into the lead-chambers. Sometimes steam is admitted into the combustion-furnace, which is said to hasten the formation of sulphuric acid. With a furnace of the dimensions stated, 26 tons of brimstone per week are said to have been burnt in a perfectly satisfactory way, corresponding to the work of 15 ordinary burners; by cutting off part of the air it was possible to reduce the sulphur burnt to 5 or 6 tons per week. For an equal chamber-space much more sulphur can be burnt than with ordinary burners without any damage to the process, owing to the even work and the avoiding of any excess of air. Indeed Blair's burner is much commended, and probably would have been more extensively employed, but that soon after its invention most large works (and only such can do with it) have passed over from brimstone to pyrites.

At the present time, of course, nobody would think of such a way of cooling the gas as is shown here in the cast-iron dome H. We would employ its heat in a Glover tower, or previously for concentrating acid. We would also replace the potting arrangement shown in the diagram by the more perfect arrangements to be described later on in connection with pyrites-kilns; or we would leave it out altogether, and supply the chambers with liquid nitric acid through the Glover tower.

A modification of the principle of burning the subliming sulphur by introducing air behind the burner was patented by H. Glover (No. 3774, 1879). He arranges behind the burner a chamber, loosely packed with bricks, in which the vaporized sulphur deposits before it can get into the lead-chambers. This brick chamber, when it is partially filled with sublimed sulphur, is burned out by admitting air into it. The heat is utilized for concentrating acid, and the gases are eventually passed into a Glover tower, where they do all the necessary denitrating work. This system is at work at a Philadelphia factory, and gives entire satisfaction, as observed by myself, no repairs having been required after the lapse of five years.

This arrangement is shown in fig. 59. A is the usual burner-plate, B the feeding-apparatus (on the same principle as used in Blair's burner); the burner-gases, with the subliming sulphur, pass into the chamber C, where they meet air entering through the pipes F, either cold or previously heated by waste heat. The mixture further passes through chamber D, containing a network of fire-bricks like that used in a Siemens' recuperator; the mixture and combustion here become perfect, and the gases, now entirely deprived of free sulphur, pass away through H and the flue IK. On their way a platinum dish, E, for concentrating sulphuric acid, is placed on the top of chamber D, and further (leaden) pans, J and G, are employed for a first heating of the acid. From here the acid gas passes into a Glover tower, where it is still hot enough to concentrate all the Gay-Lussac acid (equal to 1½ times the daily make of the chambers) up to 150° Tw., and impart to it a temperature of 127° to 132° C. The lead pans G J and platinum dish E produce daily 9000 lb. of acid of 91 or 92 per cent. H_2SO_4 from chamber-acid of about 123° Tw.; that is, two-thirds of the acid made from the 4000 lb. of brimstone burnt on plate A. Since this acid is taken directly from the chambers (the Glover-tower acid being used exclusively in the Gay-Lussac tower), and since the concentration is not driven to a higher point than 92 per cent., the platinum dish never requires any cleaning out of iron salts &c.

Another sulphur-burner, on the principle of continuously supplying liquid sulphur, is that employed at the works of M. de Hemptinne, at Brussels, and shown in figs. 60 and 61 (taken from the 'Bulletin du Musée de l'Industrie de Belgique,' January 1882, sent to me by the Author). It consists of a cast-iron arch A, strengthened by bracings, and resting on a large flanged wrought-iron plate with flat rivets which can be heated or cooled by flues underneath. On this plate there are placed, side by side and as level as possible, four cast-iron plates with 3-inch upright

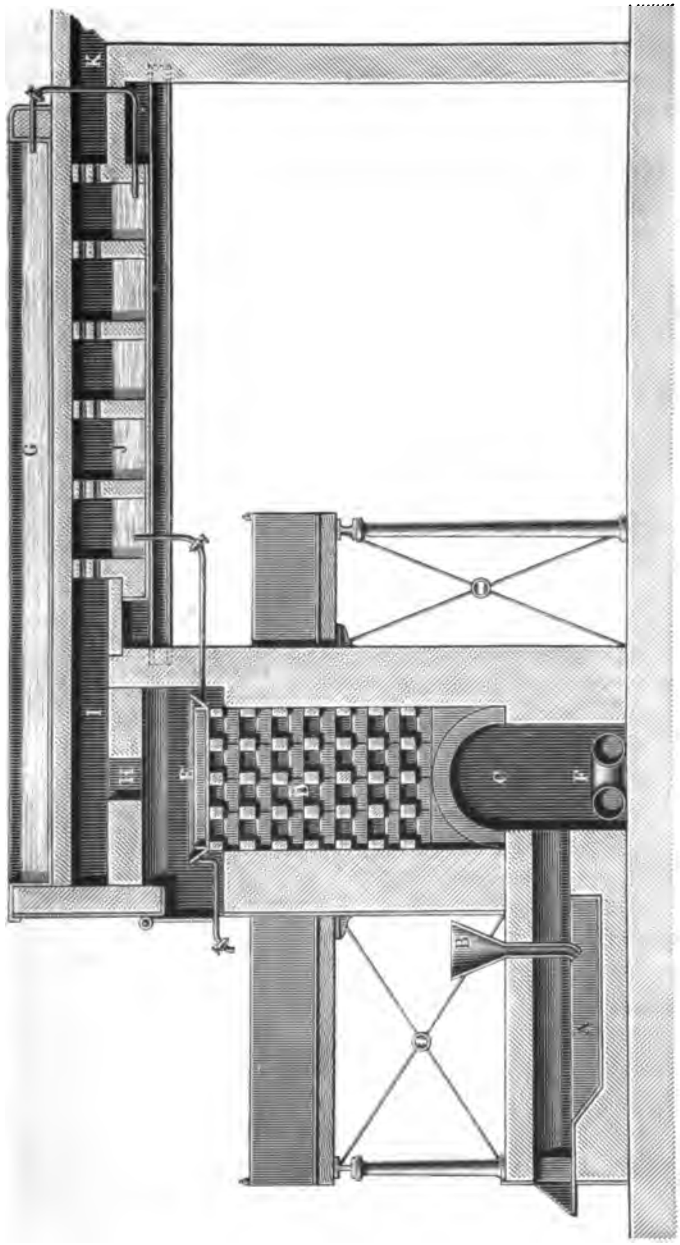


Fig. 59.

Fig. 61.

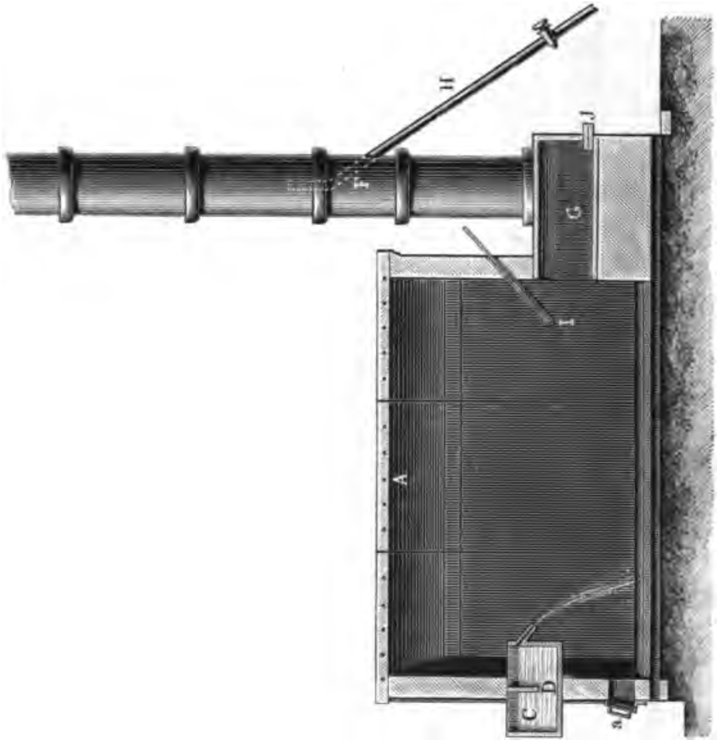


Fig. 60.

flanges, intended for burning the sulphur, which is supplied by four spouts from a cast-iron box C, divided into four compartments and built into the front wall, as shown in the diagram. Perpendicular partitions D serve as lutes for preventing the burner-gas from blowing out in front; if the combustion should spread to the front, a cover (not shown here) would at once put out the flame. Thus the supply of sulphur takes place regularly; the four hinged doors *a a* in front serve merely for the entrance of the air and for clearing out the cinders. The arch A consists of ten pieces bolted together; it is covered by light sheet-iron shutters, E E, bent to the same shape and covered with a mixture of loam and straw, which can be raised or lowered by a chain, pulleys, and counterpoises. This admits of regulating the heat of the chamber; if it rises too much, one or more of the shutters E E are raised. An alarum thermometer, I, in a copper tube, indicates the temperature. The gases escape through the metal pipe F, resting on a thick-walled cast-iron box G, from which the deposit formed can be withdrawn through J. Through H an extra supply of air can be let into the tube F. [This arrangement for supplementary combustion is decidedly imperfect.]

For producing cold and dry sulphur dioxide, free from sulphuric acid, such as is specially useful for preparing liquors for manufacturing wood-pulp, Némethy (G. P. No. 48285) recommends the combination of a sulphur-burner, cooled from the outside by water running down the sides, with a chamber, placed underneath, filled with iron borings, in which the sulphuric acid is retained. From here the gas passes through a number of flat, perpendicular, iron boxes, cooled by water running down their sides, and then into the apparatus, where it is to be absorbed by milk of lime, &c.

W. Maynard (patented as a communication to A. M. Clark, No. 6982, 1884) draws the gas out of the chamber where it is generated (by burning sulphur in cups) by means of a goose-neck pipe leading from the top of the chamber to a closed box provided with a funnel delivering into another box below. Water is discharged by a pipe into this funnel, which has grooved sides, so that the liquor running round as well as downwards forms a vortex, and draws away the vapours generated in the burning-chamber. This arrangement is evidently not intended for sulphuric-acid making, but for preparing a solution of sulphurous acid.

Fig. 62.

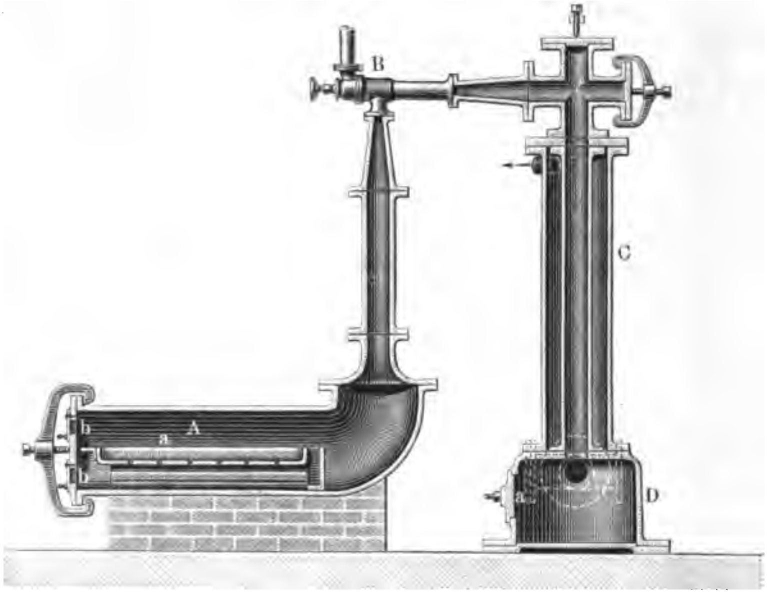
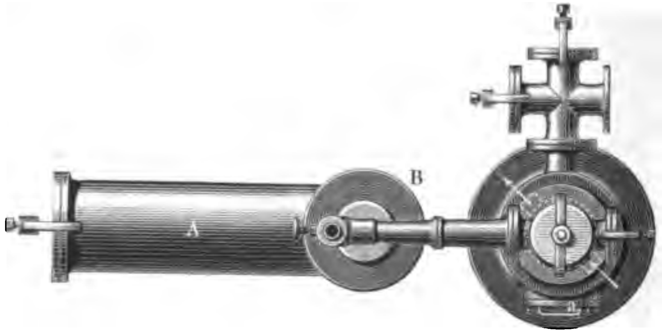


Fig. 63.



The following arrangement, by Körting Brothers, serves for preparing comparatively small quantities of sulphur dioxide from sulphur, for bleaching, in the manufacture of glue, for saturating the liquors in sugar-works, and the like. It is also used in wood-pulp works. A (figs. 62 and 63) is a cast-iron retort provided with a perforated dish *a*, in which the sulphur is placed. B is a Körting's injector, made of regulus metal (5 lead, 1 antimony), which, by means of a steam-jet, aspirates air through the holes *b b* into A and causes the sulphur to burn. The vapours are forced downwards in the inner tube of the cast-iron cooler C, whilst cold water flows in the annular space between the two tubes, entering at the bottom and running out at the top. The box D, on which the cooler is mounted, serves for retaining any sublimed sulphur and other impurities. From here a tube leads the purified SO_2 to the place where it is to be utilized.

The Némethy burners, Körting burners, and others, are especially used in Germany and Austria for the manufacture of bisulphite of lime, to be employed in the manufacture of paper-pulp (called "cellulose") from wood. A number of other burners serving for this purpose are described in the 'Papier-Zeitung' for 1894, pp. 1478 & 1830.

In Germany, in 1900, 33 paper-works made sulphite cellulose by means of brimstone, of which they consumed 15,000 tons against 33 works employing 70,000 tons pyrites. Both together made by this process 350,000 tons wood-pulp.

The following analysis of the *residue from the sulphur-burners* has been made by Richardson (Richardson and Watts, 'Chemical Technology,' vol. i. pt. v. p. 198) :—

Sodium sulphate *	13·77
Calcium sulphate †	28·49
Calcium silicate †..............	15·91
Sodium silicate..................	1·10
Ferric oxide and alumina ...	2·80
Water and sulphuric acid *...	13·05
Insoluble	24·29
	99·41

---

[*] The sodium sulphate and the free sulphuric acid (or rather the acid sulphate) evidently come from the nitre-pots boiling over.

[†] The lime no doubt partly comes from the brickwork of the furnace.

A special *cooling of the gas* from sulphur-burners for manufacturing sulphuric acid (as distinct from that of bisulphite of lime) is, as a rule, not only unnecessary, but even injurious; so that, for instance, in the furnace shown in figs. 50 to 53 the vertical metal pipe conveying the gas to the chamber had to be protected against cooling by a brick jacket. Even where no cooling takes place by water-pans, steam-boilers, &c., the gas gets into the draught-pipe sometimes at only about 100° or 120° C. temperature, which is just sufficient not to allow the nitric acid to condense before it gets into the chambers, a contingency decidedly to be avoided. Where water-tanks, acid-pans, &c. are used, the temperature of the gas is said to come down as low as 40° C.; in this case only liquid nitric acid can be used for the chambers. In Blair's or Glover's continuous burner the temperature certainly rises much higher; and in this case a cooling-arrangement, such as that described, was formerly thought indispensable, before means had been found of utilizing the heat of the gases in a Glover tower or otherwise.

B. THE PRODUCTION OF SULPHUR DIOXIDE FROM PYRITES.

1. BREAKING THE PYRITES.

The pyrites, as it comes into the market, is always sufficiently pure to make a separation from gangue unnecessary, except in the case of pyrites picked from coals ("coal-brasses," p. 41); but this is only a locally-used by-product.

It is, however, always necessary to break up the larger lumps in order to burn the pyrites completely; and this is always done at the works themselves—except in a few cases, where they buy smalls direct from the mines. The majority of the factories break the ore by hand; and it is found that various descriptions of ore behave very differently in that respect. The Norwegian ore is the hardest; here the large lumps have to be broken with great labour by means of 20-lb. fore-hammers. The Westphalian ore is much more easily broken—still more easily the Spanish and Portuguese and some of the French ores; these, however, make a good deal more smalls, 10 per cent. and more. The softest ore is that from Chessy, consisting of loosely aggregated individual crystals, which by a blow of the hammer fall to powder. Some of the Spanish ores are equally roughly crystallized; these ores are very troublesome for use as lumps.

In England the ore is generally broken so that all the pieces pass through a sieve with 3-inch holes. On the other hand, as few smalls as possible are made. The broken ore must be sifted again to separate the smalls, for which purpose some works pass it through a half-inch, others through a quarter-inch riddle. What remains on the riddle is *lumps*; what passes through, *smalls, fines*, or *dust*. Each of them has to be treated separately. It is very important that the ore be used neither in too large nor in too small pieces. In the former case it does not burn right through; there remain green cores in the interior of the cinders, which can be seen on breaking them up. These large lumps also get too hot on burning, and may cause the formation of slags (scars) by production of FeS, as will be subsequently explained. If, on the other hand, the pieces are too small, they prevent too much the access of air, and similar results follow in this as in the former case.

It is quite obvious that the pyrites-burners can be worked to full advantage only if the ore is in pieces of as uniform size as possible, and it would hence be the best plan, although it is hardly practicable in reality, to separate the broken ore into a number of sizes, to be burnt in separate kilns. At Oker formerly the ore was broken to walnut size for the grate-burners as shown later on. For deep kilns, as now altogether used there, the ore is broken into pieces of 2½ inches side. The fines, sifted through ½-inch sieves, are burned in a Rhenania blende furnace (comp. later on).

Owing to the great manual labour required for the breaking of pyrites, the same *mechanical stone-breakers* have been introduced for this purpose which originally were made for road-metal. One of these machines is that of Blake, built by Messrs. Marsden of Leeds, which is shown in figs. 64 and 65. This machine is made of various sizes, and accordingly varies in the amount of work turned out and in the size of stones it can attack. A and B are the two active parts, the "jaws." A is fast and perpendicular, B movable, and makes with A an angle of 72°, by oscillating a little round the fixed shaft D. This movement is communicated to the jaw B from the main shaft, H, by means of the angle-lever, E E′, and the crank motion, G H, so that the angle-lever presses the jaw

Fig. 64.

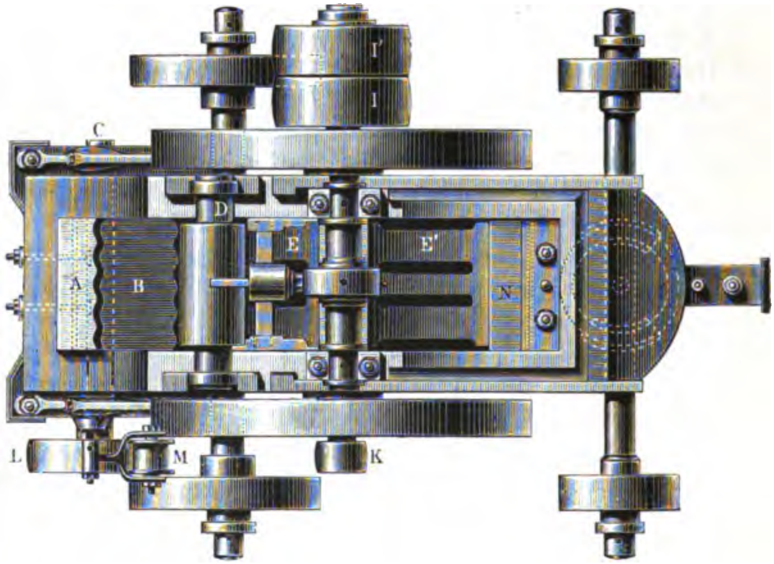
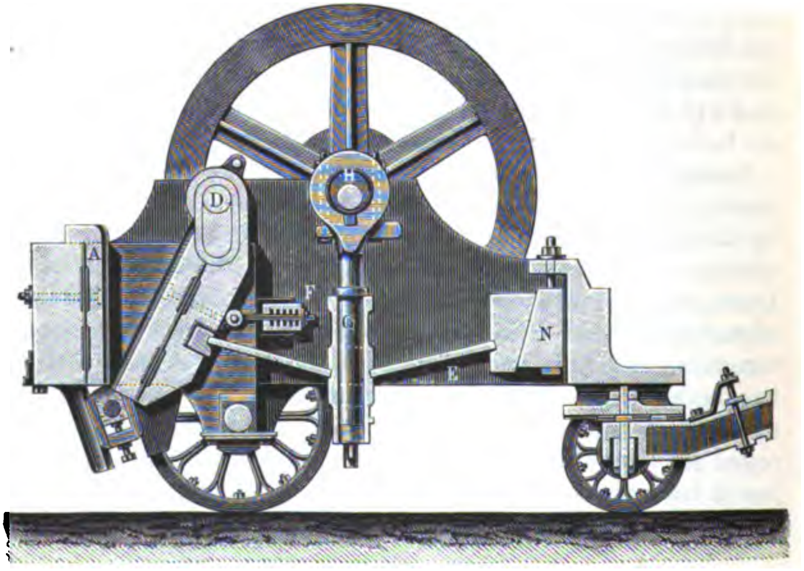


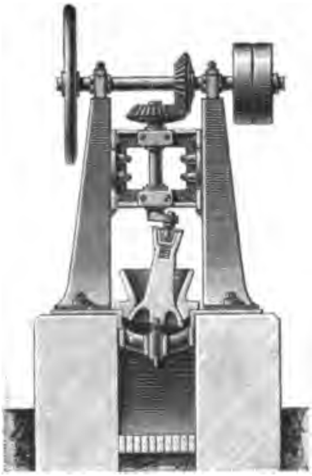
Fig. 65.



B against the stones charged, the return motion of B being caused by a spring, F, cased in india-rubber. The angle-lever is adjustable by the wedge, N, lying behind its arm E′. The roller, C, causes the broken stones to be regularly ejected; it receives its motion by a belt from the main shaft, by means of the pulleys, K, L, and the expanding roller, M. The crank-shaft, H, is also driven by a belt from the fast and loose pulleys, I I′. The machine is mounted on a four-wheeled bogie. It makes a great deal of noise and needs frequent repairs; but the jaws, which principally suffer, are so arranged as to be easily replaced.

Blake's engine has been improved by Broadbent & Son, of Staleybridge, who have replaced the spring bedded in india-rubber by a simple, easily-adjustable lever arrangement, which saves labour as compared with the original contrivance. Output, according to size, from 40 to 130 tons in ten hours; price £140 to £375.

Fig. 66.

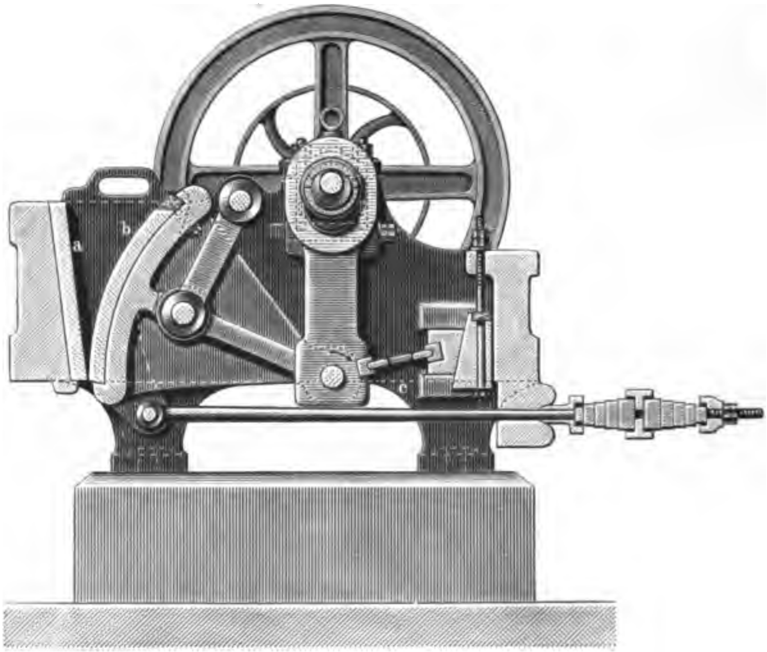


At Oker, a steam-engine of 12 horse-power drives two stone-breakers, mounted one above the other. The higher one breaks the large stones roughly, the lower one down to the proper size. They supply, in the case of very hard ore, of 2½ inches, 60 tons, with milder ore, 72 tons per shift of ten hours.

A crushing-mill was invented by Motte, at Dampreny, near

Charleroi, which has been improved by the Märkische Maschinen Fabrik (G. P., October 16th, 1877; 'Dingler's Journal,' ccxxvii. p. 58). The principle is that of a peculiar kind of mortar, with hollow bottom, in which the crushing is done by a pestle, as seen in fig. 66. Whether this mill is really preferable to the older stone-breaking machines experience will show.

Fig. 67.



Durand and Chaptal's stone-breaker consists of a number of hammers attached to a horizontal revolving shaft. It is said to make less dust than other stone-breakers. The smallest apparatus breaks from 8 to 25 tons of stone in 10 hours, with an expenditure of 2 or 3 horse-power, the larger size from 80 to 130 tons, with 6 horse-power.

Vapart's breaking-mill (address, "Chênée, Vieille Montagne") works centrifugally.

The Humboldt Engineering Company at Cologne (Germ. Pat. 1906, Jan. 12, 1878) manufacture stone-breakers which do twice the work of those formerly in use, with the expenditure of the same force.

Other improvements in stone-breakers have been invented by Brown ('Scientific American,' 1879, p. 194) and Welter (German Patent, No. 7494, March 5, 1879).

A machine very much recommended is Breuer's "Sectorator" (G. P. 30477), supplied by Ernst Maetz, Berlin, S.W. As shown in fig. 67, it contains a straight breaking-jaw, *a*, firmly connected with the solid frame, whilst the movable jaw, *b*, is suspended in two steel trunnions, and is partially revolved against the jaw *a*, thus crushing the material. The angle between the two jaws is rather acute, so that large pieces are easily caught and carried forwards towards the bottom slit. If both jaws were arched, the material, especially large pieces, would be able to escape upwards for a long time, until gradually broken up. The width of the bottom slit is adjustable by a wedge even during work, so that any size can be obtained. The plate *c* behind the excentric sheave, which is easily exchanged, is of cast-iron and of a smaller section than any other part of the machine subjected to a breaking-strain, so that in case of excessive strain by the passage of a foreign body (iron, &c.), that plate must give way before any other part of the machine.

Even at some large works they prefer dispensing with mechanical stone-breakers, principally for two reasons. The first of these is that they make more dust than breaking by hand; but since dust is now even more profitably burnt than pieces, this reason is no longer valid. The other reason is, that at large works there is always a certain number of men who are incapacitated for other work, or who are temporarily unoccupied, and these are best set to stone-breaking.

2. PYRITES-BURNERS FOR LUMPS.

Among the apparatus for burning pyrites in the manufacture of sulphuric acid, a distinction has to be made between those intended for lumps and those intended for smalls. It is indispensable to keep both kinds apart, and to employ different apparatus, or at least processes, for them; for if the broken ore is put into the burner without separating the smalls, the air-channels, which ought to remain between the pieces, are soon partly stopped up with powder, and the access of air becomes irregular; thus scars are formed and proper work is then impossible. Apart from the coarser and finer powder obtained on breaking, a great deal of smalls comes into the trade direct from the mines, obtained there by the use of water for separating the ore from the gangue.

Where cupreous pyrites is roasted without any regard to the utilization of the sulphur, the only object being the extraction of the copper, usually no regular kilns are employed at all, but the ore is burnt in "heaps." This is done on an enormous scale in the south of Spain; but the damage to health and vegetation has been so great that a law has been passed compelling manufacturers to abate this nuisance. In order to avoid the necessity of building the very large number of closed kilns which would be required for that purpose, various proposals have been made. We quote that of Fleming (E. P. 10153, 1887). Above the roasting-heap, and extending downward over the whole portion (about one-third) which emits the fumes, is suspended an iron hood, lined with tar and painted outside with a non-conducting material. The hood is supported by chains from two pairs ot shear-legs, and the whole is strengthened by iron stays. At one end of the hood is a pipe, by which the roaster gases are led to condensing-flues, to separate arsenious acid, and thence into vitriol-chambers. If the gases have excess of air, they are led through calcining-furnaces; if insufficient, more can be supplied by regulating-dampers in the flues. [Apart from all other objections to this process, the "iron hood lined with tar" is sure to be not very durable.]

The burning of pyrites in lumps (pieces) for the manufacture of sulphuric acid is always done in such a way that the combustion heat of the pyrites is utilized for maintaining the process without employing any extraneous fuel. The apparatus used for this purpose are called "kilns" or "burners." In the first edition of this work (pp. 151–154) there will be found a description of the old and now abandoned kinds of kilns, with many diagrams—as the burner originally employed by Farmer, the first shape of tall kilns without grates, the Oker kilns for roasting the Rammelsberg ores. These kilns (except Farmer's) are constructed without grates; they are still used for roasting poor ores, lead-matte, &c. In the same edition there is a description of the Belgian hearth-furnaces and of the Marseilles furnaces, both of them very faulty and quite antiquated (pp. 157 & 158). This also holds good of the various descriptions and illustrations of "Freiberg kilns," still given in our second edition (pp. 214–218). Instead of these, I am enabled, through the kindness of the respective authorities, to show the kilns used at the present day (1902) at Freiberg and at Oker, at the Government works carried on at those localities.

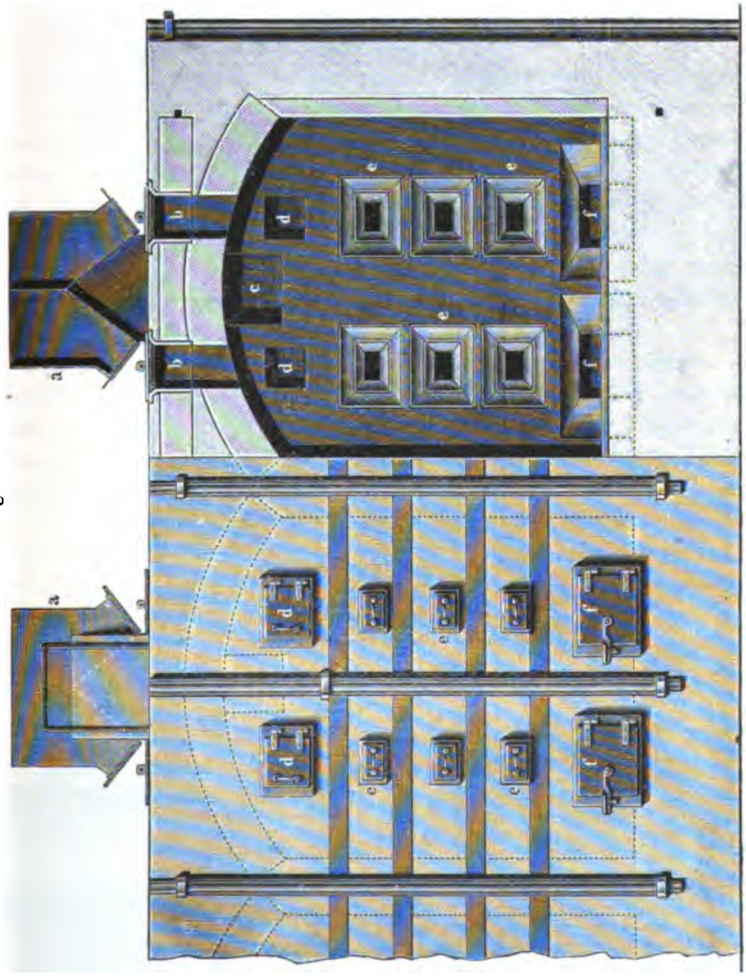


Fig. 68.

Fig. 69.

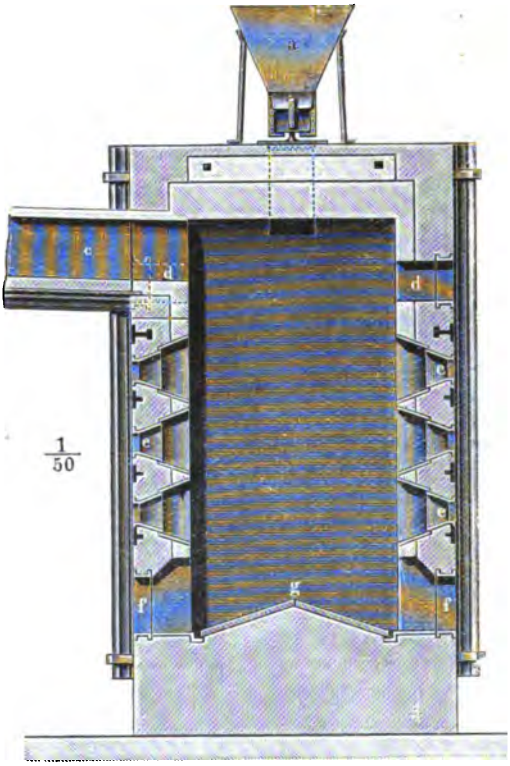
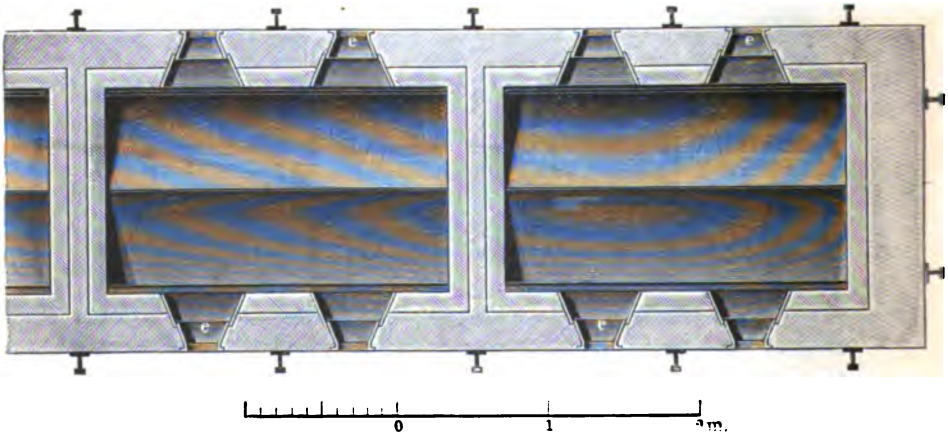


Fig. 70.



For poor ores and intermediate products which must be treated at metallurgical works (pp. 81 *et seq.*) furnaces are required of a different kind from the grate-burners now universally employed for good pyrites in lumps. The style of kilns now used at the Muldenhütten near Freiberg is shown in figs. 68, 69, 70. They serve for poor iron-pyrites containing blende and arsenical pyrites, as well as for lead- and copper-matte.

The grate formerly employed at Freiberg has been replaced by slanting cast-iron plates, *g*. The air does not now enter through special channels, but through the discharging and working holes. *a* shows the charging hopper, *b* the channel through which the charge gets into the kiln, *c* the exit channel for the roasting gases, *d* openings for spreading out the charge, *e* working-holes, *f* discharging-holes. Each kiln roasts about 25 cwt. of pyrites per 24 hours; 5 kilns are combined in a set. The sulphur is roasted off to 4 or 5 per cent. in the cinders.

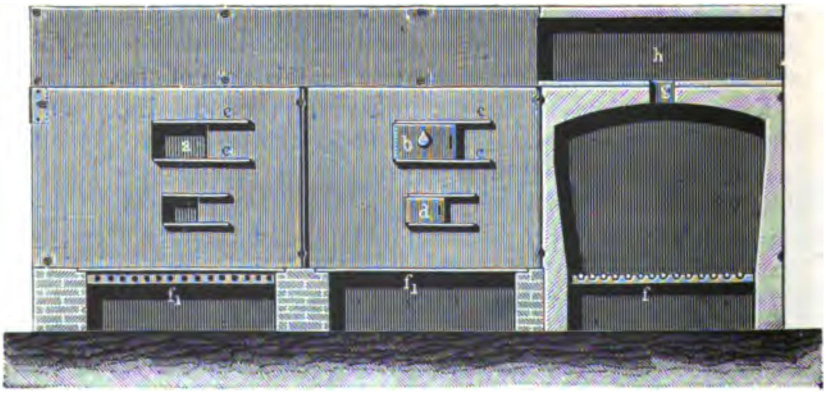
For richer and purer pyrites, at Freiberg grate-burners are employed consisting of three kilns, with 25 square feet grate surface each, and a distance of 4 feet from the movable grates to the crown of the arch. Each set roasts about 36 cwt. pyrites per 24 hours down to 2 or 3 per cent. S.

The kilns now used (1902) at Oker are exactly like the Freiberg kilns just described. They are of two different sizes—deeper kilns (with a layer of ore 9 ft. deep) serve for the poorer ores, shallower kilns (the ore lying 6 feet deep) for the richer ores (described p. 83). The English grate-burners, formerly employed at Oker, have not been found suitable for this class of ores.

Kilns of the just-described kind have been found indispensable for roasting poor ores, matte, &c., where the sulphuric acid is a by-product and where the heat generated in the process is less than when roasting ordinary pyrites, containing at least 40 per cent. sulphur, usually a good deal more, such as is now universally employed for the manufacture of sulphuric acid as a principal product. For such richer ores the kilns or burners ought always to be constructed with *grates and ash-pits.* This causes a considerable improvement in the working of the furnaces. Where the air has merely to pass through a mass of burnt ore, its quantity cannot possibly be regulated at the inlet, but only by dampers at the other end of the furnace. It is even a more serious disadvantage that in this case the subdivision of the air inside the burner must be very irregular. According to the greater or smaller resistance offered by the individual portions of the layer of pyrites, the air will pass through very unequally, and in less quantity at the places where most pyrites is lying and where it is most required. The addition of a grate and a closed ash-pit alters the state of the case at once, in this way, that only a definite quantity of air need be admitted into the ash-pit, and that, moreover, this air must first spread equally underneath the grate and rise all over the area of the burner. Thus the ore is much more completely burnt, and at the same time richer gas is obtained, which leads to a better chamber-process, higher yield of acid, and smaller consumption of nitre; the operation of drawing out the burnt ore becomes much more regular and offers a greater guarantee against raw ore getting into it; lastly, it does not happen so often that fused masses ("scars") are formed in the burner, although also in the case of grates this easily happens if the method of working is faulty.

The introduction of grates led to further improvements—to begin with, a diminution of the height of the burners, which made them much handier for working, and which acted especially well with more easily fusible ores, although in some places the other extreme of too low layers of pyrites has been resorted to.

Fig. 71.



The different kinds of grate-burners which were introduced into England about 1860, and have been employed up to this day both there and in many factories abroad, are shown in figs. 71–75.

Figs. 71, 72, 73 show a somewhat simple construction, which can be made with open sand-castings; figs. 74 and 75 a more expensive kind of front plates, requiring planing, turning, &c.: the latter are much neater and cleaner, because no putty is required for the doors. Sometimes these front plates undoubtedly become a little warped, and then the doors are not tight without putty.

Fig. 72.

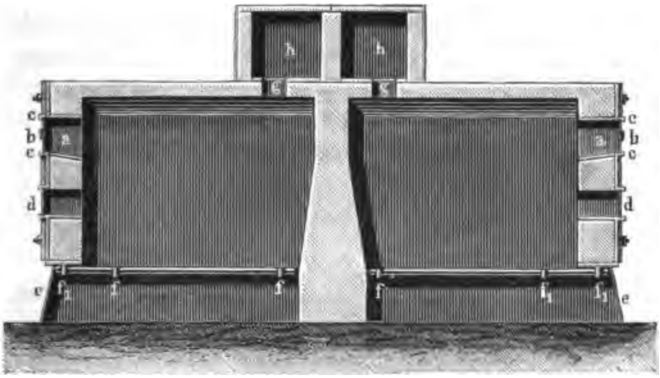
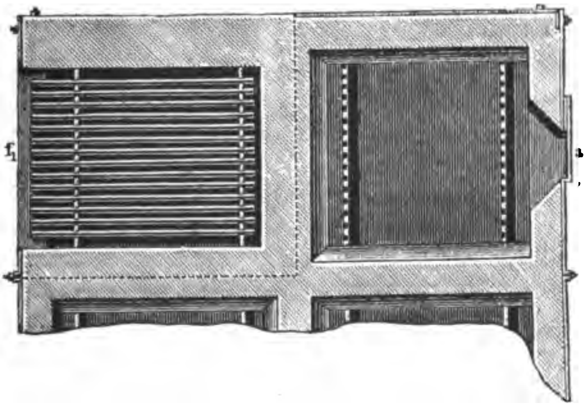


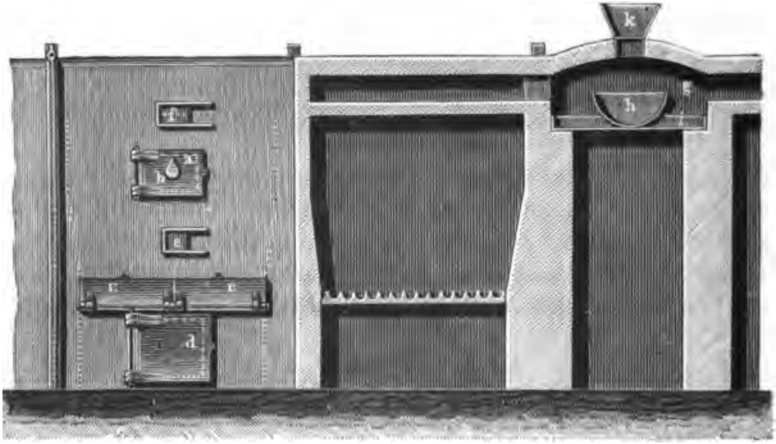
Fig. 71 shows two burners in front elevation and one in section, the first burner without doors. Fig. 72 is a cross section, showing two rows back to back; fig. 73 a sectional plan, half taken just over the grate, half through the middle of a door. *a* is the working-opening, with the door *b*, which slides in the grooved ledges, *c c*,

Fig. 73.



cast to the front plate. The small door *d*, only to be used exceptionally, is arranged in precisely the same way. The openings of the brickwork inside are protected by small metal plates; *e* is the movable cover of the ash-pit, provided with air-holes; *f f* are the grate-bearers; the front bearer f_1 at the same time carries the bottom plate for the front wall, and is perforated with round holes; while *f f* are cut out in semicircles. The arches are sprung parallel with the working-doors, and, by the draught-holes *g g*, are in connection with the gas-flues, *h h*. The latter, like the burners, are cased in metal plates; they are covered with fire-tiles.

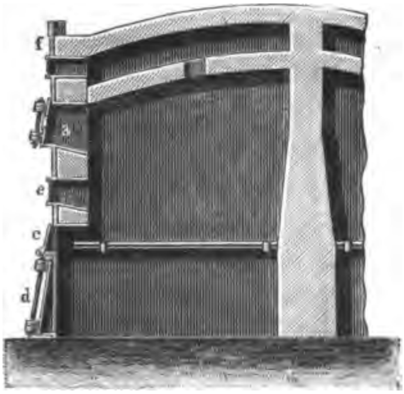
Fig. 74.



A somewhat more costly but more perfect arrangement is shown in figs. 74 and 75, in front elevation and two sectional elevations. *a* is the working-door, with the small slide *b* for observing the interior of the burner; it turns on hinges, and, as shown in fig. 75, lies on a projection of the front plate, slanting forward towards the bottom; all the metal parts coming into contact are planed and faced, so as to close air-tight. The doors *c c* for the grate and *d* for the ash-pit are constructed in the same way, whilst the rarely used doors *e* and *f* (the latter for the gas-flue) are made in the simple manner shown in fig. 71. The burners are supposed to be the last of the row; so that the nitre-oven *g*, with the semi-cylindrical trough *h*, the saucer *i*, and the hopper *k* are immediately joined to them. The diagrams are all on a scale of 1 to 50.

English pyrites-burners generally have a moderate area of grates, about 4 or 5 feet wide, and 4½ to 6 feet from front to back. The inner walls sometimes rise quite perpendicularly; more frequently the two sides and the back slant a little outwards, up to the level of the working-door, to the extent of about 9 inches, sometimes only 6 inches, in width, and half as much in the back; from that level the walls rise again perpendicularly up to the roof. The front wall, which is only 9 inches thick, and mostly protected by a 1-inch or 1½-inch metal plate, rises perpendicularly, and is perforated with several working-holes. The ash-pit has either vertical sides or, more rarely, sides converging towards the bottom, in order to facilitate the removal of the cinders. Its depth varies from 16 to 24 inches. The level of the working-doors, which determines the depth of the layer of pyrites, varies from 1 foot 8 inches to 2 feet 6 inches; but the former depth is considered by most English acid-makers too little, at any rate for average ores, and they prefer a depth of between 2 feet and 2 feet 4 inches, but nearer the higher than the lower limit. In Germany, the depth of ore is only 1 foot 6 inches, even down to 1 foot 4 inches (comp. p. 305). The reason for this is the fear of scarring, which English experience with the same ores proves to be unfounded. The height from the upper level of the ore to the abutment of the arch is usually about equal to that of the working-door, say 9½ to 12 inches, and from there up to the crown of the arch another 8 or 9 inches. The arch itself is either sprung from side to side, as is the custom on the Tyne

Fig. 75.



(whereby the walls are made to bear the weight more equally and the working through the doors is facilitated), or, as is usual in Lancashire, from front to back (which is more advisable in the case of two rows of burners being built back to back, in which case the arch is sprung over both burners together, with a supporting wall in the centre). In any case it is advisable to build the burners back to back, even with arches sprung from side to side, wherever it is locally possible; thus one back wall is saved, the heat is kept up better, and a common gas-flue can be employed.

The *gas-flue* of the English burners is always at the top, each burner-arch having a hole of 4 to 5 inches square leading into it. These holes are not always provided with dampers; but by gradually increasing the size of the whole as the distance from the main shaft becomes greater, evenness of draught is produced. The flue itself can be made of bricks set in tar and sand, and covered with fire-tiles. Most modern works prefer forming it by a second arch, about 6 or 12 inches above the burner-roof, reaching right across the whole burner, and supported by the front plate being made high enough.

The principal feature of the English pyrites-burners, which is used in all continental works as well, except in some burners for metallurgical purposes (Mansfield or Freiberg kilns), is the employment of *grate-bars* of square or oblong section, movable in bearings, and leaving larger or smaller spaces between them, according to their position. (According to Hasenclever, in Hofmann's 'Bericht,' 1875, i. p. 158, movable grate-bars have been used in France ever since 1848.) Fig. 76 represents such a grate-bar, showing also the parts which are forged or cast round, so that they can easily turn in the respective hollows of the bearers. Bars 2 inches square are usually made of wrought iron; the oblong bars, 2 by

Fig. 76.

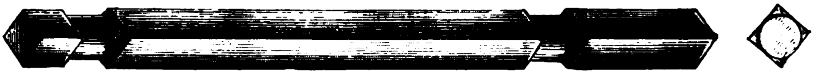
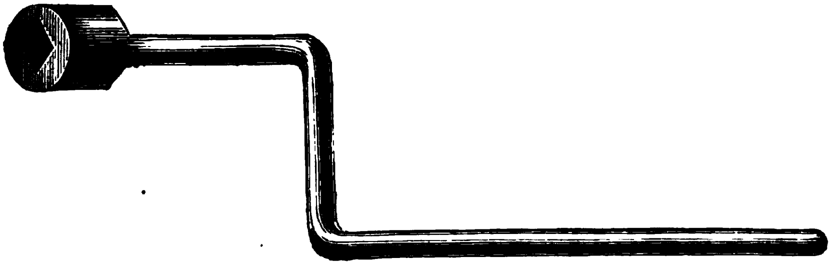


Fig. 77.

3 inches, which, being turned on edge, leave a larger space, and therefore only suit larger pieces, are mostly of cast iron. The grate-bars rest on cast-iron bearers, as shown in fig. 77; in the shallower kilns (4½ to 5 feet from front to back) there are two such, in the deeper kilns (5 feet 3 inches to 6 feet from front to back inside) three. According to this, of course, two or three rounded places must be made on the bars themselves. Lest these should be weakened too much, the diameter of the round parts in the square bars is equal to the side of the square, in the oblong ones equal to the smaller side. In any case the front piece of each bar, where it projects beyond the bearing-bar, remains square or oblong, so that it can be turned round its axis by means of a suitable key (fig. 78). The intervals between the grate-bars are mostly managed so that with 2-inch bars they are about 2 inches when the bars are in the situation shown in fig. 79; but if they are turned 90 degrees, as in fig. 80, the intervals will only amount to 1¼ inch. In another actual instance the diameter of the bars was 1¾ inch, the clear distance in the straight position 1½ inch, in the diagonal position 1 inch. If, lastly, the situation is as in fig. 81, where half of the bars are turned, the intervals will be between the two above limits; and as each bar can be turned separately, many combinations can be produced. Usually the bars stand as in fig. 80—that is, all with their diagonals in a horizontal plane, or with the smallest possible intervals, so that the pieces of ore cannot fall through. As soon as a portion of the ore has to be removed, the attendant takes hold of the front end of the bar with his key, and moves it a few times from side to side. Thus a kind of crushing action will be exercised on the cinders getting between the two bars, the intervals are momentarily enlarged, and

Fig. 78.

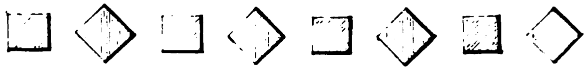


the cinders jammed between the bars are forced downwards. Of course great strength is required for this work. At the same time, by the action of the key, the pyrites is loosened up to a certain height. The workman now goes from one bar to another, generally missing one, and shakes them, according to his perception, so far that an equal quantity of burnt ore is drawn out all over the area of the grate. That which has fallen through is allowed to lie in the ash-pit till the time comes, once every 24 hours, for opening the bottom door and taking away the cinders. A new shape of bars, which was said to possess great advantages over the ordinary angular ones, was patented by W. Helbig (Dingl. Journ. ccxxvii. p. 67) and is shown on p. 222 of our second edition, but omitted here, as it seems to have found no practical application. It was a cast-iron bar with a worm-thread all round it.

Fig. 79.

Fig. 80.

Fig. 81.



A burner patented by Harlan & Grenshaw (G. P. 100,243) contains hollow grate-bars, with tapering, narrow chambers, rising vertically nearly to the top of the layer of pyrites, so that the air enters not merely at the bottom above the grate, but also higher up, nearly to the top of the pyrites.

Dr. Burgemeister (private communication) employs bars made of a cruciform section. When turning these round, the smaller pieces easily fall through; the larger lumps get between the bars and either pass through on turning back or are crushed. The following diagram shows the different positions of the bars:

+ + + +
× × × ×

It is a great improvement (but rarely met with, because it necessitates a somewhat complicated plant) if the *ash-pit* is deep enough for introducing an iron bogie below the grate whose top equals the whole surface of the grate in size ; the ash-pit door, of course, must be correspondingly large. The cinders in that case fall direct into the bogie, and can be wheeled out in a few moments ; usually they have to be raked out by hand, during which time the door must stand open, and much false air gets into the burner. Where there are not two rows of burners built back to back, it is possible to charge on one side and discharge on the other ; but there is not much advantage in this arrangement, which takes a great deal of space.

The *discharging of the burnt ore* (*cinders*) is sometimes expedited by iron bogies running on tramways, which are introduced into the ash-pits, and into which the cinders fall as the grates are shaken. This very suitable plan necessitates a system of tramways and turn-tables, as well as a lowering of the whole floor. The following simple and equally efficient plan seems therefore worthy of recommendation. It is a *tilting-box* (figs. 82 & 83). There are two independent parts :—first, an iron box, of suitable dimensions, with two outside pivots near the upper edge ; secondly, a light but strong wheeled frame, which ends in forks fitting under the pivots. As shown in the diagram, the whole is used like an ordinary iron wheelbarrow on any hard ground. But by lifting up the handle the box is first lowered to the ground, then the forks slip out and the frame can be run back. Similarly the box is taken up again by running the frame in, and depressing the handles till the forks take hold of the pivots. The boxes can be made to fit into the ash-pits, and the cinders discharged into them directly from the grates. Of course other applications of this barrow will present themselves in chemical works.

In order not to be obliged to open the whole ash-pit when shaking the bars, all the best furnaces are provided with a slit in the front plate, through which the ends of the bars are accessible. Except whilst the bars are being shaken, the slit is covered by a door, which is best made in two halves.

Norrington (E. P. No. 4131, 1878) makes the ash-pit doors to slide in horizontal frames, and connects all the doors of a set of burners by jointed rods, so that they can all be moved together in a horizontal plane by means of an endless screw and gearing at one end. All the ash-pit doors are thus opened and shut at the same time. This is always done whenever any one of the working-doors is opened so that no gas can blow out, as the air cannot enter in any other way. According to information from Messrs. Charles Norrington & Co., Plymouth, this arrangement effects a considerable saving of nitrate of soda and of sulphuric acid; owing to the regularity of draught, all kilns burn equally well. This statement is confirmed by Dr. Ballard (Report to the Local Government Board, 1879, p. 180).

Fig. 82.

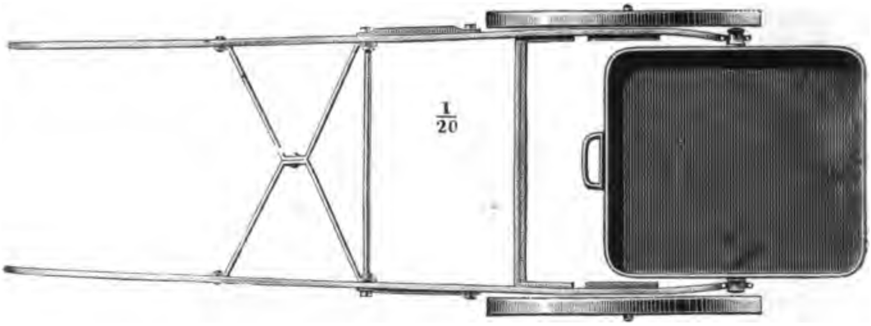
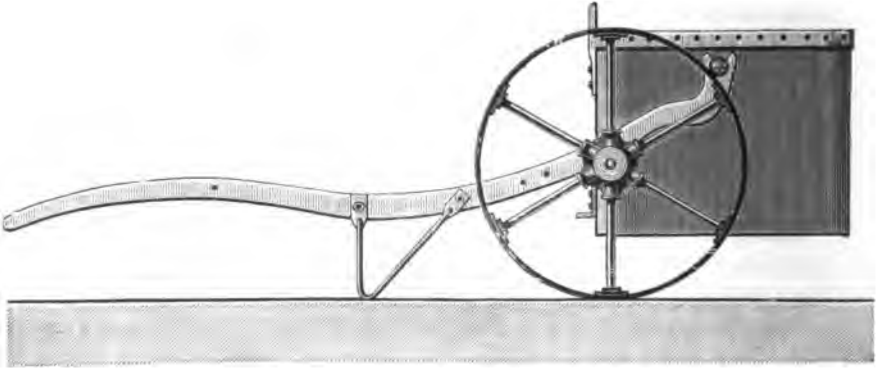


Fig. 83.



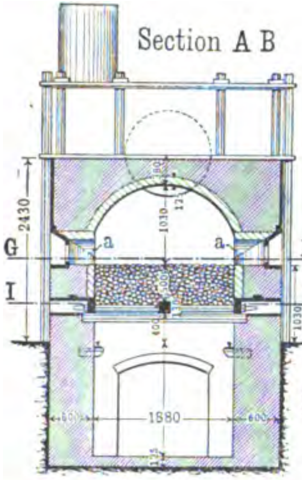
According to a communication from Mr. K. Walter, a simple means of preventing the blowing out of gas at the working-door during charging is this: to arrange a flue underneath the burners, in connection with the chimney, which is opened during the charging just sufficient to prevent any blowing out at the working-door. Less gas is lost and less nuisance is produced in this way than is otherwise the case from the working-doors. With this arrangement the ash-pits require only loosely put-on wrought-iron doors.

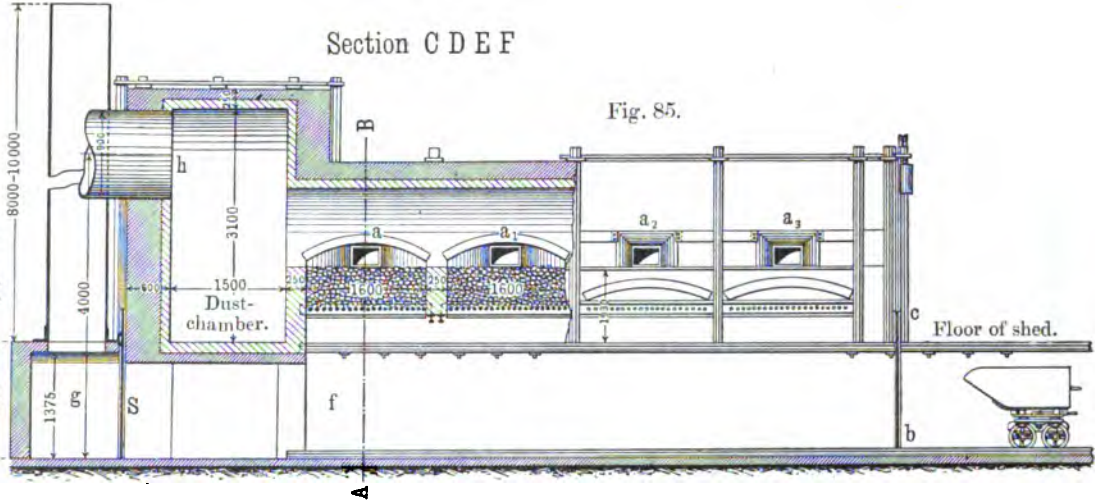
In England it would probably not be allowed to discharge the gas into the chimney, even for a short time: this objection is overcome by the following plan :—

Hasenclever (Chem. Ind. 1895, p. 494) describes the following arrangement for preventing any escape of gas from the burner-doors into the working-shed during the time the doors are open for charging. In some cases the chambers are placed high enough over the burners (say, at least, 18 feet above the floor) to secure sufficient draught at all times; but even then the false air entering during the time of charging may be troublesome in the lead chambers. The device proposed by Jurisch (Ueber die Gefahren für die Arbeiter in chemischen Fabriken, p. 37) that a by-pass should be made from the burners directly into the chambers, which should be opened by means of a damper every time a burner is charged, is altogether impracticable, and is evidently not practiced anywhere. The difficulty, however, is solved by connecting, during the time the kilns are being charged, the ash-pit (by means of a special flue) with a chimney producing but little draught, so that no burner-gas is drawn downwards into the flue and the chimney, but the burning of pyrites in the kiln is interrupted.

This is done at the Rhenania Chemical Works by means of the arrangements shown in figs. 84–87, which, at the same time, illustrate the form of burners (p. 299) frequently employed on the Continent, where the burners have a common gas-space, the pyrites lies on the grate in rather shallow layers (19½ inches), and the cinders are removed by means of bogies run underground into the ash-pit. The burner-gas in the ordinary way passes from the dust-chamber through pipe *h* into the Glover tower. Each time the cinders are let down into the ash-pit by shaking the grate-bars, damper *b c d e* (fig. 86) is shut down, so as to close flue *f* against the outer air, but not hermetically, and damper S is opened, which leads through *g* into a chimney, which is *not* connected with any furnace, and is only 25 or 30 feet high, so that it just projects over the roof of the shed. The small quantity of air which enters round damper *b c d e*

Fig. 84.





Front elevation.

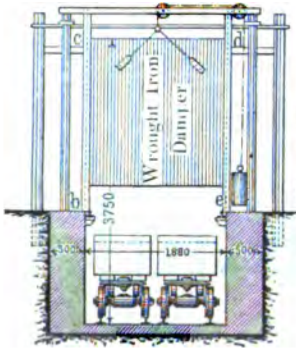


Fig. 86.

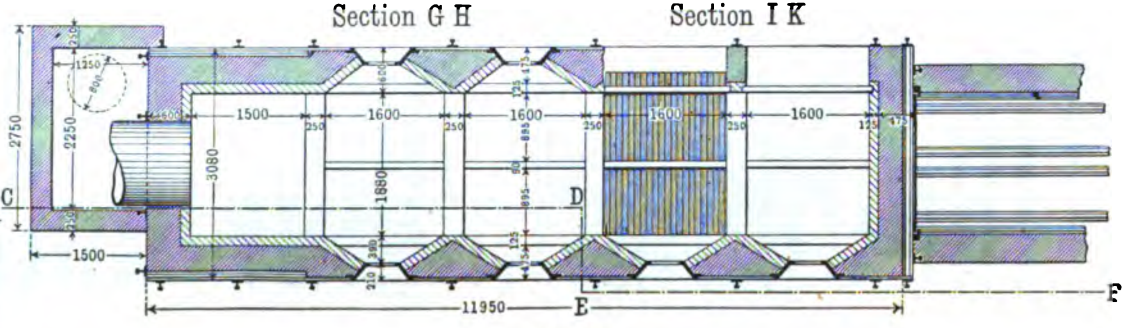


Fig. 87.

is partly drawn into this chimney, and the pyrites consequently burns so slowly that no gas issues from the doors *a*, a_1, a_2, a_3. The men now charge the burner with fresh pyrites through these doors, shut the doors, let down damper S, and raise damper *b c d e*, whereupon the evolution of sulphur dioxide recommences, and goes on all the more regularly the more burners are united in the same set. Experience has shown that no sulphur dioxide is drawn down into *f g* during the operation, so that none can escape through the special chimney.

The Stassfurter Chemische Fabrik, vormals Vorster & Grüneberg (G. P. 100,708), arranges a flue connecting two sets of burners, or the single burners of a set, below the level of the grates. In this case, when the charging-doors of one burner are open and those of the other burner are shut, the air-openings below the grate being shut in both, the second burner will draw its supply of air from the first, through its open doors, so that no gas will blow out of these.

In properly constructed pyrites-kilns, all *doors* for charging, working, shaking of the bars, and getting out the cinders either run horizontally in grooves, or, still better, they are hung on hinges; and the door-frame, cast upon the front plate, is made to slant forwards below, sometimes also sideways, so that the door lies fast upon it by its own weight. As both the door-frame and the edges of the door touching it are planed, the doors close tight without any luting, whilst those running in grooves must be made tight with lime-putty.

All *brickwork*, so far as it is affected by the heat (that is, the walls above the grates, the arch, and the gas-flue), is lined with fire-bricks; the total thickness in front is one brick, behind (or as the partition between two rows of burners) two bricks. The side walls dividing each two burners of a row are 1½ or 2 bricks thick, but they diminish upwards to one brick. The roof need only be 4½ inches thick. The mortar is fire-clay, as usual; in the colder parts, such as vertical gas-shafts, flues, &c., this does not stand so well as boiled-down tar and sand.

F. J. Falding (Min. Ind. vii. p. 666) constructs the first layer behind the cast-iron front plates of hollow bricks, so that air-channels are formed from the grates upwards to the top of the burner. This keeps the burner-room cool and easier to work in, at the same time retaining heat for concentration in acid pans on the top of the burners, or for increasing the efficiency of the Glover tower, or for supplying the burners themselves with hot air, which is an advantage in some cases.

Of course the burners are well bound together, either by special uprights and tension-bars, or by flanges cast to the front plates, provided with holes for the cross-bars (fig. 73).

Opinions as to what *size* the burners are to be made vary a good deal. Mostly smaller burners are met with, about 4 feet 6 inches to 5 feet from the outside to the inside of the back wall. The reason given for this is that longer grates cannot be served so well, and that in a larger burner the newly-charged ore forms too shallow a layer (the depth of the whole layer of pyrites, including the partially burnt ore, is not in question here). I have, however, worked for a good many years with larger burners, nearly 6 feet from the front to the back end of the grate, and have burnt my ore better than the majority of other works using the smaller burners. Certainly, the usual 7-cwt. charge had to be all put in at once, whilst in the smaller burners it is introduced in two halves every 12 hours; and many practical men assert that a 12-hours' is preferable to a 24-hours' charging; but this is not borne out by experience. It is, however, a decided mistake to try burning a much larger charge on the larger grate, say 8 or 9 cwt. This can only be done with poor ores, such as are not in use at the present day, except locally; richer ores, especially those containing copper, are sure to be fluxed by the heat getting too high, and cause the greatest trouble. As a result of long experience, I am inclined to consider a grate-surface of 4 feet 6 inches by 5 feet 8 inches, and a depth of pyrites of 2 feet 3 inches, very favourable for burning 7 cwt. of 48-per-cent. Spanish ore, changing once every 24 hours.

The rate of burning just mentioned equals 30 lbs. of 48-per-cent. pyrites per superficial foot of grate in 24 hours. With poorer ore (40 to 42 per cent.) I have certainly burnt in the same grate 8 cwt. (=35 lbs. per square foot), and with 38- or 40-per-cent. ore even 9 cwt. (= nearly 40 lbs. per square foot). In England the maximum quantity of pyrites burnt per square foot of grate will very rarely exceed 40 lbs. of 48-per-cent. pyrites; reliable figures from one of the largest works are 35½ and 39 lbs. But in German works, according to Hasenclever, using Westphalian pyrites, the proportions are 41·6, 44·5, 57·8, 60·3, and 65·0 lbs. (Wagner's Jahresb. 1871, p. 212). Bode (*ib.* 1874, p. 245) quotes for

Westphalian pyrites of 41 or 42 per cent., 50·7 to 64·0 lbs.; for Norwegian ore of the same strength, 38·3 lbs.; for Valais ore, with 35 per cent. sulphur, up to 92 lbs. per square foot in 24 hours. Favre (Monit. Scient. 1876, p. 271) states as the most favourable ratio in his experience 55·3 lbs. of 40-per-cent. pyrites per square foot in 24 hours.

At the Oker works, in 1901, the roasting area of the three deep kilns (p. 295). serving for a chamber set of 5289 cub. metres amounted to 33·55 superficial metres, that is 0·00634 sup. met. per cub. met. of chambers. The quantity of ore roasted per square metre in 24 hours was 0·45 ton copper-ore, 0·50 ton pyritic lead-ore, 1·40 ton copper-matte, 1·60 ton lead-matte (comp. p. 83 on the composition of these ores).

In 1902 the Rhenania works at Stolberg considered 200 kils. Westphalian pyrites per superf. metre grate-surface as the normal quantity; with 230 kils. the degree of desulphurization was somewhat less. The former is = 40 lbs., the latter = 46 lbs. per superf. foot.

In England some thirty or forty years ago many pyrites-burners were made about 33 inches wide and 26 inches from front to back at the fire-bars, but 42 inches square at the level of the bottom of the charging-door, giving a slope of 6 inches back and 9 inches sideways. Later on burners were made larger, say 39 × 42 inches at the bars and 48 × 51 inches at the charging-doors, many going up to 54 inches wide and 60 or 66 inches from front to back at the fire-bars. The smallest sizes burn about 4 cwt. of Spanish ore = 44 lbs. per square foot in 24 hours; the largest sizes 7 cwt. = 31 lbs. and upwards per 24 hours. The most usual size is about 16 to 18 square feet at the fire-bars and 22 to 24 square feet at the base of charging-doors, burning 7 cwt. daily = 37 to 41 lbs. of ore per square foot. This is about the maximum for rich ores consistent with proper freedom from fluxing, but poor ore may be burned in larger quantity (Thorpe's Dict. of Applied Chemistry, iii. p. 719). With the very well-burning Aguas Teñidas ore Davis (Chem. Engineering, ii. p. 124) states the proper charge = 2·3 lbs. per square foot per hour = 55 lbs. per day, in which case the cinders tested 1 per cent. S.

It is hardly necessary to say that the pyrites-burners are always built in *sets*. Usually 12 to 24 burners are served by the same set of men; and they must be worked so that every one gets its regular turn, as is evident from the necessity of a regular evolution of gas. Frequently the burners are built underneath the acid-chambers. Not only must they in any case be protected against rain (if not underneath the chambers), but they must not stand in a space open at the sides, since strong winds would put their draught wrong, and cause them either to go too fast or to blow out at the doors. It is best to protect them by light walls or by a brattice with shutters adjustable according to the direction of the wind.

As the drawings of the English burners (pp. 298 *et seq.*) show, each burner is independent of the other, and they do not communicate one with another, but only with the common gas-flue. Each burner, then, ought to have its own damper, which is not always the case. On the Continent, frequently the single burners are separated merely by low walls; the ore in this case lies only about 18 or 20 inches deep on the grates, and the whole set is like one large burner with a divided grate (p. 306). It is, of course, not possible, as on the English system, to treat each burner individually, to give it more or less draught, to isolate it for repairs, &c. Nevertheless this system is in favour with some of the more experienced Continental manufacturers, who say that 18 inches depth is quite sufficient for the rich ores, now universally employed, and that the connection of the gas-space of all burners into one whole is preferable to the English system, because one burner can aid another and the whole is visible at a glance. Evidently this system, of which good illustrations are given in figs. 84 to 87, p. 306, answers its purpose as well as the English; and in a special case, in which I saw a set of English burners working alongside a set of burners of the kind just described, the manager informed me that he preferred the latter, because it was easier to regulate the draught than with the English burners.

In Continental works possessing no Glover tower it is usual to concentrate the chamber-acid up to 144° Tw. in *lead pans*, which are mounted on the top of the burners, and are heated by their waste heat. Of all plans for concentrating sulphuric acid this is, as we shall see later on, the cheapest, only excepting the Glover tower. There is no reason why such pans should not be placed on the English burners as well; but even before the Glover tower did away with most lead pans, the above arrangement does not seem to have been practiced in England, where, however, the space on the furnace-arch is otherwise usefully employed for drying "balls" from pyrites-dust, &c. There are also, as we shall see in Chapter IX., sometimes reasons against placing the pans on the top of the burners.

The *"potting" of the mixture of nitric and sulphuric acid* (liquid nitric acid is not used in England for this purpose) is now nearly always done in such a way that the burners are not disturbed by it. Twenty years ago the pots were frequently put on pillars between two burners, with a common gas-space; these were provided with special potting-doors in the burner-front, and cast-iron dishes as saucers for receiving the stuff that boiled over; these saucers were inclined towards the doors, so that the nitre-cake could not so easily run into the burners; but it got out of the doors, which made them look very dirty; and ultimately it also got into the burners themselves. None of the better factories have this arrangement now, but all pots belonging to a set of burners are placed in a separate "nitre-oven," which is nothing but an enlargement of the gas-flue, and either situated over the burners or on pillars outside the same. The latter is preferable; for also here there is always a metal saucer provided for catching the boiling-over nitre-cake; this may be cracked before it is noticed, and much nitre-cake may get into the burners, doing great damage. If the arrangement is similar to fig. 74, p. 298 (where, by the way, the nitre-pots are replaced by a better contrivance to be subsequently described), no risk of the above-mentioned kind is run.

Favre ('Moniteur Scientif.,' 1876) reports that the works in the south of France use pots of 2 ft. 7½ in. × 1 ft. 6 in. × 12 in., standing on a bridge between two burners; and he also mentions the drawback of boiling over into the burners. This would show that those works, even in 1876, were in a backward state.

Special kinds of Pyrites-burners.

Addie (E. P. 180, of 1886) describes a peculiar pyrites-burner. It consists of a cupola, brought to a white heat, in which the pyrites is charged together with sandstone or other slag-producing material, and is burnt by a hot blast, the cinders being reduced to a molten slag which is run off from time to time. Unless this apparatus was intended for some very special purpose, not apparent at first sight, it must be pronounced as very impracticable so far as the chemical manufacturer is concerned.

The methods described in the patent of Hargreaves, Robinson, and Hargreaves (E. P. no. 5681, 1886) for treating pyrites are evidently less intended for the manufacture of sulphuric acid than for the recovery of arsenic, antimony, copper, silver, and gold. A whole set of burners is combined in such a way that the air or the gaseous products at first formed can be successively passed through them in regular rotation. The air, previously heated in recuperators, passes downwards, first through nearly exhausted ore, afterwards successively through ore containing more sulphur. The residual ore is treated with acid gases, in order to bring the metals into a soluble state. For details we must refer to the patent specification.

Burners for roasting copper-matte.—Haege (Berg- u. Hüttenm. Zeit. 1893, p. 383) describes the process introduced by him at Britonferry, near Swansea. The copper-matte produced there could not be roasted in Mansfeld kilns, nor in ordinary pyrites-burners. The desired result was obtained by increasing the heat, in the first instance by a suitable treatment of the matte, and in addition to this by improving the construction of the burners. The matte was rendered porous by tapping it on to a sand-bed slightly moistened and dusted over with fine coal. It was then crushed by a Blake's stone-breaker, in which one of the corrugated faces had been substituted for a smooth one, so that flat, more tightly lying pieces were obtained, which were separated from the smalls by a riddle with meshes of ⅜ inch width. The burners are of the ordinary shape of English pyrites-burners, described above, but of slightly different dimensions:—Grate-surface 4 ft. 3 in. by 4 ft. 4 in.; area at the level of the upper working-surface 5 ft. by 4 ft. 9 in.; height from grate-bars to the upper working-surface 2 ft., to spring of the arch 3 ft. 4 in., to the crown of the arch 3 ft. 8 in.; smoke-flue at the lowest point 6 in., at the highest 1 ft. 4 in.; total outside height 7 ft. 10 in. The heating-up takes place from the top, exactly as described in the text; the burners are ready for work in two or three days. Each burner then receives a charge of from 6 to 7½ cwt. of crude matte every 12 hours. After three hours everything becomes red-hot, after six hours a bright cherry-red heat is attained. Now the interior of the burner is worked up through the middle door by means of a steel poker, 2½ in. thick, pointed at one end; any lumps formed are broken up; and this working over is continued through the upper door. After another two or four hours the heat is at its maximum; the upper working-door is now mostly at a dark-red heat. Then the heat decreases. 11½ hours after charging the grate-bars are turned and shaken, in order to remove the roasted matte, and after 12 hours a new charge is made. There is no picking out and recharging of imperfectly roasted matte, since everything is well finished. The draught must be well regulated; there should be a slight plus-pressure within the burner. In this way mattes containing from 20 to 47 per cent. copper are treated. The poorer matte yields rather hotter and better gas and more sulphuric acid than the richer. With 20-per-cent. matte the roasted product contains 9 per cent. sulphur, with rich matte it contains 11 per cent. sulphur; both are at once ready for the concentrating work. From 40 per cent. matte about 47 or 48 per cent. of the weight of roasted matte is obtained in the shape of chamber-acid of 110° Tw., with consumption of 0·8 to 1·0 nitre per cent. of chamber-acid. The gases are hot enough to thoroughly decompose the mixture of nitre and sulphuric acid in the nitre-oven and to denitrate the acid in the Glover tower; the acid flows from this with a temperature of 140° to 155° C.

Working of the Pyrites-burners for Lumps.

In order to *start a burner* it is first, if newly built, dried by a slow fire in the usual way, and then filled with burnt ore to within 3 inches below the working-door. If no burnt ore can be procured, ordinary road-metal, &c., may be taken, broken sufficiently to pass between the grate-bars when they are turned. The draught-hole of each burner is closed by a damper, and the working-door is left open. Then ordinary fuel (wood or rough coals) is heaped on the ore and lighted. After twelve or twenty-four hours the burner and the uppermost layer of the ore will have reached a dull red heat; the rougher parts of the fuel still present are then drawn out and an ordinary charge of green pyrites is put on. By the heat of the burner-walls, that of the ore below, and the fuel still present, the fresh ore will soon be lighted; when it is fully burning, the working-door is closed, the damper closing the access to the gas-flue is opened, and the gas allowed to go to the acid-chambers. Care must be taken in lighting up not to go too far, which would damage the burners.

Thus the process is started; and it is now continued regularly and uninterruptedly till it has to be stopped for external reasons. Repairs are very rarely necessary in pyrites-kilns; but those of other parts of the acid-making apparatus may compel their stoppage. At some English works the dampers are put in every Saturday at midnight, and are opened only on Sunday at midnight; in the meantime all other openings are well closed; and the burner thus keeps its heat so well that the new charges at once take fire when brought in. If any temporary interruption of work does not last beyond four or six days, usually the burners can be kept hot enough in this way to be started without any fresh lighting-up by means of fuel.

The regular burning-process has a double object, from which follow all the precautions to be observed. In the first place, the sulphur contained in the ore is to be burnt as far as possible; and, secondly, a just sufficient quantity of air is to be employed, no more and no less than is required for the chamber-process. This means, besides the air necessary for burning the sulphur to sulphur dioxide, as much more air as is required for oxidizing the latter to sulphuric acid, and, moreover, a certain excess of air found necessary in practical work. Anyhow, therefore, the air will be more than just sufficient for burning *all* the sulphur contained in the pyrites; and the second condition seems thus to imply the first. But this can be said only for brimstone and for pure pyrites not containing any zinc-blende or galena, &c.; for only the former can be desulphurized completely by their own heat of combustion. The sulphates of iron, which are always partly formed as intermediate products, are decomposed again at a comparatively low temperature into Fe_2O_3, O, and SO_2, or into Fe_2O_3 and SO_3, for which the heat of the burners is quite sufficient. This is a little more difficult with the sulphides of copper; but the temperature of decomposition of $CuSO_4$ is also within a red heat. Moreover the copper-extraction works do not want all the sulphur to be burnt, but allow a residue of from four to at most six per cent. sulphur in the cinders. If, however, the ores contain blende or galena, which on burning are transformed into zinc and lead sulphates, the burner cannot possibly effect a total desulphurization; for these sulphates are only decomposed at a strong white heat, which is not allowable in a pyrites-burner, and they must thus remain as such in the cinders. Furthermore, if the pyrites contains calcium sulphate or carbonate, a corresponding quantity of $CaSO_4$ will remain in the residue. Any barium sulphate present would not be taken notice of in the testing of the pyrites or the cinders, being classed among the "insoluble."

In the case of the usual description of pyrites, not containing any considerable quantity of zinc or lead, the burning of ore in lumps will reduce the sulphur in the cinders with good work to 3 or 4 per cent. Less than 3 per cent. of sulphur rarely occurs on an average of the whole year; but with very good ores it may go down to 2½ per cent. At the Rhenania works, at Stolberg, even pyrites with 6 or 7 per cent. Zn is burnt down to 2 or 3 per cent. S, exceptionally 4 per cent. (information received in 1902). Most frequently the limit stated above for good work is exceeded; some works leave 6 or 8 per cent. of sulphur, and even more, in their cinders, whilst their neighbours only leave 4 or 5 per cent. in the same ore. The fault of this may be due either to the description of burner employed or to the style of work. If, by the construction of the burner, the pyrites lie in too shallow a layer, and this is let down too soon on shaking the bars, it will easily come out badly burnt. But even if the burner is correctly built, much still depends upon the skill and care of the burner-men.

Excellent results are obtained with some of the very rich descriptions of Spanish non-cupreous pyrites recently come into the market (p. 56). These pyrites can be burnt down to 0·5 per cent. of sulphur in the cinders, so that the latter can be sent straight to the blast-furnaces. But if this degree of purity is to be obtained, the place in front of the kilns, where the burnt ore is drawn out, must be kept perfectly clean, so that no green ore can get mixed among the cinders; and any portions of these which have been spilt from the discharging bogies on to the ground must not be shovelled back into them, as they will have some admixture of dust from green ore, but they must be put back into the kilns.

How much depends upon employing the ore in *neither too large nor too small pieces*, and upon keeping the pieces of as *uniform a size* as possible, has been mentioned on p. 287. Only then will it be possible to regulate both the depth of layer and the draught in a satisfactory way.

Whether pyrites is properly burnt or not can be recognized to a great extent by the eye. By the burning-process the pieces swell out and burst in some place; they become light and porous, and assume the red colour of ferric oxide, in the case of cupreous pyrites a more blackish-red colour. The burnt ore ought therefore to consist of light porous pieces of the proper colour, apart from the powder always present in large quantity, which is generally sufficiently burnt off. Already, on taking up the larger pieces, their weight will allow a rough judgment of the state of the burning; and this can be more distinctly recognized by breaking the pieces and observing whether they contain a raw core in the centre. Also the presence of many slags (scars) on the cinder-heap is a proof of bad burning.

Important as these empirical signs are, no well-managed factory will be satisfied with them, but will from time to time, daily or at least twice a week, have the cinders tested, after having drawn a large sample and reduced it properly. At all events the above-mentioned empirical signs have hardly any value for small ore.

The chemical testing of pyrites cinders (*burnt ore*) can take place by exactly the same methods as described in the second Chapter for the analysis of pyrites itself. It is there shown that in the case of burnt ore more expeditious methods may be used, and that among these that of Watson-Lunge (igniting with sodium bicarbonate and titrating the undestroyed sodium carbonate) seems to be the most accurate (p. 76).

The sulphur contained in the burnt ore is no longer in the shape of FeS_2, apart from any quite raw cores in large pieces. But even fine or quite porous cinders, burnt as well as possible, also those from pure pyrites free from lead, zinc, and lime, always contain sulphur; and as this cannot be in the shape of FeS_2, the question can only be whether they contain FeS or sulphates of iron (most probably basic ferric sulphates), or both. According to Scheurer-Kestner and Rosenstiehl (Bull. Soc. Chim. 1868, ix. p. 43), the cinders contain essentially FeS; they give two analyses—(i.) of properly burnt ore, (ii.) of an operation carried on too hot, so that the ore had fluxed. Both are from Sain-Bel pyrites, containing 46·1 per cent. sulphur in the pieces and 49·28 in the smalls.

		I.		II.
Moisture		1·0		
FeS		8·5		27·2
Fe	5·4		17·3	
S	3·1		9·9	
Oxide of iron		72·0		62·4*
Fe	50·4		41·0	
O	21·6		21·4	
Quartz		18·5		10·4
		100·0		100·0

From these analyses, it would appear that there would be no ferric sulphate whatever in the residues, which is very improbable, as such can be proved by washing with water (comp. Bode, Dingler's Journal, ccxviii. p. 327, and further analyses by Phillips, Gibb, Bräuning, Wedding, and Ulrich in the Chapter treating of the recovery of copper from the cinders).

According to Troost, the first reaction is $3FeS_2 = 2S + Fe_3S_4$. Regnault holds that the sulphide formed has the formula Fe_5S_6. Lemoine (Fischer's Jahresb. 1899, p. 355), from observations made in a Malétra shelf-burner (see *infrà*), believes that in the upper layers there is always a distillation of sulphur, which afterwards burns with a blue flame. Lower down this is no longer the case, either because here most of the pyrites is already reduced to FeS, or because the temperature is too low and the supply of oxygen too great for the formation of free S. Ferric oxide appears only after roasting for 2¼ hours. The action on pyrites seems to proceed from the outside, where there is combustion into Fe_2O_3, and the heat acting on the inner part produces a decomposition into FeS and S. The S distils and burns outside, the FeS is oxidized by the Fe_2O_3, which is again reformed by the outer air.

Richters (Dingl. Journ. cxcix. p. 292) gives the following analysis of burnt ore from the Silesia works at Saarau :—

Water	4·35
Iron	43·36
Manganese	0·16
Silica	13·92
Carried forward	61·79

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* The calculation does not agree here; 62·4 Fe_2O_3 would contain 43·68 Fe.

Brought forward	61·79
Alumina	4·84
Lime	0·02
Zinc oxide	8·83
Sulphur trioxide	4·35
Sulphur	1·53
Oxygen and loss	18·64
Nickel and arsenic	traces
	100·00

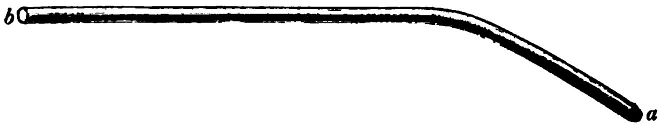
Phipson has published the following analysis of residue from Irish pyrites ('Chemical News,' vol. xviii. p. 29):—

Zinc oxide	5·50
Cupric oxide	2·86
Manganese oxide	1·60
Nickel and cobalt oxide	0·12
Cadmium oxide	0·01
Lead oxide	1·67
Antimony oxide	0·04
Ferrous oxide	1·17
Alumina	3·25
Sulphur	2·60
Thallium	traces
Indium	traces
Gangue	15·00
Ferric oxide	65·99
Lime	0·11
Magnesia	0·08
	100 00

All that has been said (*cf.* p. 315) respecting the maximum of sulphur in the cinders to be aimed at, only refers to the burning of pyrites proper—that is to say, of ores containing essentially FeS_2, and got exclusively as a raw material for vitriol-making, in which case the cinders are as good as worthless. Just in the same line are those cupreous pyrites (with less than 4 per cent. of copper) whose copper can only be extracted by the wet process; for these the above-mentioned rules for the sulphur in the cinders are equally valid. But the case is quite different with a number of ores where the residue from the burning is regarded as by far the most important product, and where the gas is only a by-product, often only converted into sulphuric acid in order to get rid of it. To this category belong blende, copper-pyrites, coarse metal, &c. Here the burning-down to the above-mentioned minimum of sulphur is partly not possible, partly not even desirable (as for copper-pyrites); and there exist for each case definite rules, which, however, do not belong to the domain of acid-making, but to that of metallurgy. Even where a larger percentage of sulphur is required for further metallurgical operations, it is more rational, so far as concerns the acid-maker, in order to save labour, burner-space, &c., to burn the material as well as possible, and to supply the necessary sulphur afterwards by adding a little green ore; thus, for instance, the copper-extraction works proceed when they receive the cinders too far desulphurized. The case of zinc-blende is a special one and will be dealt with later on.

We now pass on to the second fundamental condition of proper work in the pyrites-burners, viz., *that neither too little nor too much air be employed.* At this stage we leave out of consideration the absolute quantity of air required, and only treat of the practical rules and of the appearances observed in the burners themselves. If too little air is admitted, whether from too few holes in the bottom door being opened, or from the damper in the draught-hole not being enough drawn, or because the pipes are stopped up with dust, or the draught in the whole chamber system is insufficient from one cause or another, the same thing will happen as with sulphur-burners when they get too hot: *sulphur* will *sublime* as such, and will be deposited in the flues, the dust-chambers, the Glover tower, or the chambers themselves. It is, however, a more frequent and serious consequence that, in the case of insufficient draught, the often-mentioned *slags* or *scars* are formed. These, as Scheurer-Kestner and Rosenstiehl have shown (*l. c.*), consist mostly of *iron monosulphide,* FeS, which is necessarily formed when FeS_2 is heated, with exclusion or insufficient supply of air, along with free sulphur. It is easily fusible, and fluxes in the burners to more or less large cakes or scars, upon which the air has practically no action. The FeS fluxes all the more easily, as in the case of insufficient supply of air, where no cooling by the excess of air takes place, and more heat is developed in certain places than when the supply of air is abundant. The scars mostly enclose some green pyrites, and in this way cause a further loss of sulphur. A much greater loss is occasioned by their stopping the passage of air, so that the ore above and below a scar is very incompletely burnt. The heat is locally increased and driven further down than it ought to be; the zone of combustion is removed further downwards; and on letting down the ore the pyrites partly comes out incompletely burnt. If scars have formed in the burner, they naturally descend as the cinders are let down, and they would ultimately lie immediately on the grates and entirely stop them up. This, however, must be prevented by all means. A careful workman always breaks up the surface of the old ore before putting in a fresh charge; and thus he finds out whether any scars have formed, which mostly takes place near the surface: they can then be easily brought to the surface by means of hooks and pulled out at the door. But if they have been overlooked at first and have got lower down, in doing which they constantly increase in size, their removal is more difficult. Then a very large and heavy poker of the best tough iron (these are made up to 12 feet long and 2 inches thick), bent in the way shown in fig. 88, is introduced into the burner through the charging-hole, and the men work it till they have got the point *a* underneath the scar. Several men, working at the end *b*, then try to lift up the scar, in spite of the resistance of the superjacent mass of pyrites. This labour is very disagreeable, exhausting, and difficult. The middle doors, between the charging-door and the grate, found in all pyrites-burners, are only used in extreme cases.

Fig. 88.



With the low burners mentioned on pp. 305 & 310, where the ore lies only at a depth of 20 inches, scarring is next to unknown, at least if the ore is very carefully sized, so that all passing through a ½-inch riddle is kept out. This agrees with the facts which will now be explained.

Apart from other causes, the supply of air in a burner may be insufficient because the ore lies too deep. As the depth of the ore depends upon the vertical distance between the grate and the working-door, it follows that for ores behaving very differently in this respect differently built burners must be used. Thus the deep burners built for Irish pyrites had at once to be given up when Spanish pyrites began to be used. With the same height of pyrites which was just right for the poor ore, in order to keep the heat better together, the rich cupreous ore, in itself more fusible, became far too hot, and, moreover, the air could not pass through quickly enough to make a *complete* burning of the ore possible at every point; from both causes combined followed this effect (easily comprehensible after what has just been said), that the scarring became excessive. It is always much more feasible to burn poor ore in a shallow than rich ore in a deep burner.

Insufficiency of draught, if very considerable, will be easily recognized by the gas blowing out of all the joints of the burners, and especially coming out in force whenever the working-doors or the bottom door are opened. On the other hand, the draught should not be so strong that too much air will get into the chambers; the gas ought to be kept as rich as possible, as will be shown hereafter. It may be assumed that the draught is just right, if, on opening the small slide in the working-door, neither gas nor flame issues from it, nor, on the other hand, the flames inside the burner perceptibly tend towards the draught-hole. They ought to rise up perpendicularly and quite steadily; and on opening the door they may even tend slightly towards it. As, however, the exact regulation of the draught can only be effected by regulating the holes in the bottom door, and as on each opening of the doors above or below the grate much more air must get in than is necessary, of course the times during which the doors are opened are restricted as much, and the charging, shaking of the grates, and discharging are managed as quickly, as possible. It is very advisable to close the holes in the bottom door completely while the top door is open, or to proceed in the way described on p. 303 *et seq.* If the draught is not very copious, whenever the door is opened, there will be no room for so much air rushing in, in consequence of which a portion of the gas will rush out and get into the burner-house; this is both a loss and a nuisance to the workmen, and, in greater quantity, also to the neighbours.

For regulating the supply of air several plans are possible. The regulation takes place either *before* the grate, by the holes in the bottom door, or *behind* the grate, by means of the damper in the draught-hole or that in the large chimney behind the chambers, or else by fan-blasts (comp. Chap. V.). Regulation behind the burners is only available where all the burners have a common gas-space; otherwise the draught through the chimney or fan must be equal to the maximum amount required for all the burners, and must be changed according to the atmospheric conditions, each burner being regulated separately. This could be done best and most safely by the dampers in the draught-holes connecting each burner with the gas-flue; but these are rarely used for this purpose; they would have to be made very tight-fitting, and then would easily be set fast by flue-dust. Therefore here also the draught is made sufficient for all eventualities. The real regulation of the air, at least generally in England, takes place by means of the holes in the ash-pit door, of which a sufficient number are closed by plugs or otherwise. Scheurer-Kestner went so far as to pass all the air through a Combes' anemometer; but this can only have been done for isolated experiments, since such a delicate instrument can hardly have been kept fit for use for any length of time in an atmosphere thus exposed to acid vapours and to dust. It is therefere left to the burner-men to open or close the holes in the door as required. At the Rhenania works (1902) they regulate the supply of air, apart from the exit damper, merely by a slide damper, shutting off the flue below the grates in which the cinder-bogies are placed.

The supply of air is usually regulated by the following practical rules:—At the beginning (that is, immediately after making a fresh charge) the burner does not require very much air, till the ore has caught fire, which will take half an hour or an hour. Then more air must be admitted, always with the above-mentioned restriction—that the flames rise perpendicularly, and tend slightly towards the slide when this is opened. When, however, the principal portion of the sulphur is burnt and the flames become scarce, the air is altogether shut off, and further action is left to the heat of the burner. About two hours before it is time for recharging, the working-door is opened and the ore is well raked and turned over by means of a hook to a depth of 3 or 4 inches, and any small scars are removed. If herewith blue flames appear to any extent, this proves the burning not to have been sufficient, and a little air must be admitted. When the whole time is up, be it a twelve-hours' or a twenty-four hours' turn, the air is entirely shut off at the bottom, the small doors covering the grate-bars are opened, and the latter are turned two or three times, leaving each alternate one out. During this the workman must look through the working-door, to see whether the layer of ore is let down evenly all over; he can easily manage, determined by the eye, not to let the ore down too much or too little. Then, as quickly as posible, the new charge of ore in pieces (usually with a little dust), which must have been lying ready in front of the burner, is put in, and the process begins again. It is evident that there must be a regular rotation, so that a fresh burner comes in turn every hour or so; this is both indispensable for a regular evolution of gas, and convenient for distributing the labour over the day.

The burner-men ought to shake the grates quite equally for the purpose of discharging, so that the ore does not come down more quickly in one place than in another, and to take care that only cold, thoroughly exhausted cinders, but no red-hot ore, comes down. They ought then to work up the ore on the top through the doorway with their pokers, and rake the surface so as to make it even again. Then they must charge the new ore equally all over, starting about two inches towards the door from the back and the sides. Two men can attend to a set of 18 or 20 burners, consuming from 6 to 8 cwt. of pyrites each every 24 hours, including the wheeling away of the cinders and the potting.

The interior of a burner, after the throwing-in of a fresh charge, is, of course, at first quite black. Gradually small blue flames appear, which become larger and more lively and cover the whole mass. After a few hours they become scarcer again; but the mass in the meantime has become red-hot. Later on it cools again; and towards the end of the period there is no glowing visible at the surface; but as soon as the mass is stirred up the glowing appears again.

The men like to employ a practical test, to convince themselves that the burner is not too hot for recharging, in the shape of strokes made with brimstone on the burner-door: so long as these take fire at once, the burner is still too hot; only when they remain is it cold enough for charging. Frequently it is necessary to wait a short time, even for a few hours, after shaking the grate-bars and letting down the burnt ore, in order that the burner may cool a little before recharging it; this has the advantage that the top layer, by turning it over, is caused to burn its sulphur more thoroughly than it can be burnt after cold pyrites has been thrown in.

Generally it takes some time before the men get used to a new kind of burner or of pyrites. If even skilled men are taken from other places, they require special supervision, and still more if a new kind of pyrites has to be tried. If at all possible, different kinds ought not to be tried mixed up, but one kind adhered to for some time, because only in this way do the men get used to a thoroughly proper treatment of the burner. Each kind of pyrites requires a little different treatment as to supply of air, breaking up, &c.

An extremely great help in regulating the burning-process is the *analysis of the gas*, which, however, is nearly always made for a whole set of burners together in their common flue. We shall enter into the details of this later on.

If a pyrites-burner is working properly, it will, if touched outside, be so hot in its upper part (say 6 inches below the working-door) that the hand cannot be borne upon it; further down it must be cooler; and immediately above the grates it ought to be cold, or at most hand-warm. *This is one of the most important practical signs of the proper working of the burner.* If a burner is too hot below, this may be due to insufficient draught, or (which in the end comes to the same thing) there has either been too much pyrites charged or there is too much dust in the burner, which has stopped up the interstices. Too much dust may come from bad riddling, from too much having been added on purpose, from the falling of the "balls" inside the burners, or from the decrepitation of "explosive" ores (comp. pp. 55 & 77).

In any case, the first thing to be done, apart from removing the cause of the evil, is to again *cool* the excessively hot burner. Above all, *more air* must be admitted; and, in order to drive up the heat more certainly, the new charge must be kept back a little, and no fresh ore put in the middle, but only along the sides and the back of the burner. It always takes one or two days, sometimes longer, before a burner has recovered its normal temperature. In specially obstinate cases there is nothing for it but making very small charges for a day or two, till matters have come right again. Some manage by taking out the ignited top layer, allowing it to cool a little, and putting it back into the burner, which in the meantime has received more draught, owing to the lower depth of ore, and thus has become cooled.

If a kiln is allowed to go too hot for any length of time, whatever may be the cause (want of air, too large charges, stopping up by dust, bad breaking up), the consequence will always be the same, viz., increased *scarring*, with all its unpleasant accompaniments. I have had to deal with cases where the scars became so abundant that the burner had to be put out, the grates had to be drawn, the whole of the stone taken out, and the burner freshly filled up.

Of course it also sometimes happens that a burner goes *too cold* and the fresh charges take fire too slowly. This may be caused equally by a want of draught or by too small charges, and can be easily remedied in either case. If it has, however, got so far that the new pyrites will not take fire at all, nothing remains but to put in very hot ore from some of the other working-burners ; in this way the matter may always be put right with some patience, unless large scars are lying on the grates, or there are other serious faults, which must be removed before the burner can be expected to work properly. A frequently used but objectionable remedy against cold burners is to put live coals on the pyrites. Carbonic acid is a great enemy to the chamber process, probably not so much by diluting the gas (for its injurious action is far too great to be attributed to that alone), as by lying in the lower part of the chambers and preventing contact between the chamber-gas and the bottom acid, till it is removed by diffusion. This point, however, is not yet cleared up.

A pyrites-burner may also go too cold if there is *too much draught*—if, therefore, besides the air required for its intense working there is an excess, which only acts as inert cooling gas. This is a very great fault ; for in this way the consumption of nitre is increased and the yield of sulphuric acid very much diminished. Long before the burners cool from this cause, an excess of air may become injurious in this way ; and by observing the flames in the burners (much better, however, by the analysis of the gas), it must be ascertained whether the proper proportion of air is present or not.

Balard reports ('Rapports du Jury International,' 1867, vol. vii. p. 29) that in the first trials of Perret and Olivier for employing pyrites in manufacturing sulphuric acid, they at last succeeded in properly conducting the combustion, but obtained a very small yield of acid. They ascribed this to an insufficient draught, and applied a fan-blast; but the yield instantly became minimal. Now the other extreme was tried—the air-channels were quickly stopped up with boards covered with sheep-skins and fastened by stays. At once the chamber process became regular, and the key to employing pyrites in the manufacture of sulphuric acid was found. Probably the previous endeavours of Clément-Desormes in this respect were frustrated by his allowing too much air to enter.

Some have objected to the employment of *damp* pyrites (Kerl-Stohmann's 'Chemie,' 3rd ed. vi. p. 197), because in this case, on burning, more sulphates are formed, which give off sulphur trioxide; this takes up moisture, and condenses as sulphuric acid before getting into the chambers, destroying the flues and so forth. Even with dry ore in damp weather similar phenomena are said to be observed, and a smaller yield is alleged to be the consequence of the moisture in the air. On my own part, I have never noticed such an effect of damp weather, nor have I been able to learn anything about it elsewhere, in spite of numerous inquiries. It is very desirable that this point should be specially examined. The formation of sulphur trioxide, as well as the occurrence of liquid sulphuric acid, in the connecting-tubes has certainly been established; but it has not yet been proved that the moisture of the air acts in a way to increase that formation, and the contrary is more than likely for the formation of SO_3.

He who has no practical acquaintance with the matter, looking at these numerous sources of mishaps, may be inclined to think that the working of a set of pyrites-burners is a most difficult task. But it is far from that. If once the burners are in order, they remain very long so if the burner-men know and perform their duty to any considerable extent, and if proper supervision is exercised over them; the pyrites-burners then give even less trouble than sulphur-burners. Certainly, when they do get wrong, it takes energetic and experienced management to put them right again.

It will now hardly be necessary to explain in detail why there are only narrow limits for each given burner and style of charging, within which the *quantity* of pyrites charged may vary (comp. pp. 308 & 309). If too much is charged, the burner scars; if too little is taken, it gets cold. When, therefore, for any reason the daily quantity of pyrites has to be cut down, it is necessary to put out a corresponding number of kilns and to fully work the remainder. Only in the case of brief temporary interruptions is it possible to charge rather less than usual for a few days; but I would recommend even in this case rather to allow the bulk of the burners to go on as usual, and to keep the necessary number hot without fresh charges by closing all openings. Then these kilns will be much more easily put in order by the assistance of the other burners in full work than if they had *all* cooled down.

3. BURNING PYRITES-SMALLS.

We have seen above (p. 287) that the fine powder which passes, say, through a ½-inch or at most a ¼-inch riddle must be kept out of the ore going into the ordinary pyrites-kilns. The "smalls," "fines," or "dust" produced in this way, whether it be on breaking the ore at the works or already at the mine, must be dealt with separately.

This can be done in very different ways, according to circumstances. Where pyrites-smalls are not bought as such, the question is only about the dust arriving along with the bulk of the ore and also that made in breaking. Much more dust is made when breaking by machine than by hand—in the former case up to 20 per cent. with middling hard ores, and even more with soft ores. Formerly, before rational and really satisfactory contrivances for the burning of smalls were known, some large works, which had already mounted stone-breaking machines, went back to hand-breaking, in spite of its costing three to six times as much, merely in order to avoid the excess of dust. This was especially the case with works using soft ores, such as the Tharsis ore; with Norwegian ores the advantage was always on the side of the mechanical breaking, because these are much harder and make less dust. If the quantity of dust going through the smaller riddle does not exceed 1½ cwt. to the ton, it can be got rid of, according to my own experience, without any special contrivance, in the following way:—The dust is sifted off as usual, and a certain quantity of it is laid down for each burner alongside the pieces. If, for instance, the whole charge is 7 cwt., 6½ cwt. of pieces are used and ½ cwt. of dust; if more than this is used, the burner easily gets out of order. First the coarse ore is charged as usual; and then the man throws the dust with his spade along the *sides* and the *back* of the burner, leaving the whole central part free. Anyhow, the ore ought to be levelled with a hook, after throwing in the charge, in such a way as to make it higher along the sides and back than in the centre of the burner. The reason is this: the air entering from below meets with much less resistance at the comparatively smooth walls than in the centre of the layer of ore, and it will preferably rise along the former; the centre thus will get less air than the parts next to the walls. If, however, the latter lie at a higher level, and especially if the passage of air is obstructed by the dust lying at those places, the draught will be more nearly equalized, and the burning will take place evenly all over the area of the burner. Of course it is not well to proceed too far in this way; nor can it be expected that the result is as good as when lumps and smalls are each treated in the best way suited for them.

The arrangement just described does not answer if more than 1¼ cwt. of smalls to the ton of pyrites has to be dealt with; and special arrangements must then be resorted to. Probably the oldest method, now almost obsolete, is the following:—The small ore is, without further grinding, mixed with sufficient clay to make it plastic, made into a puddle with water, formed into *balls*, and dried on a steam-boiler or pyrites-burner. Rarely less than 10 per cent. of clay will be required for this, often more, up to 25 per cent. The balls are then charged along with lumps into the ordinary burners, but never too many at a time (at most one-sixth part of the whole charge), because they fall to powder in the burner after a time, and if used in a greater proportion would stop the draught. Only locally is such rich clay found that the balls stand pretty well in the burners and can be well burnt off. The workmen dislike them very much, because they disturb the working of the burners, even when the above-mentioned restriction of their quantity is observed; if a burner is not quite warm, they must at once be left off. Some, in order to get rid of them without disturbing the burners, burn them by themselves, mixed with "coal brasses,"—that is, the pyrites picked out of coals, which always retains some of the latter, and therefore burns more vividly and gives out more heat than pure pyrites; but then it sends the injurious CO_2 to the chambers. Usually not much is gained by making the balls with clay, since they so quickly fall to pieces in the burner; and nearly as much can be done by throwing the dust at once into the burner and saving the cost of making the balls. Only by a very strong admixture of clay can the disintegration of the balls be prevented; but then the loss of sulphur and the contamination of the burnt ore is all the greater. In both cases the sulphur left in the burnt ore rises very much, from 6 to 8 per cent. and more. Where the cinders go to copper-extraction works, the use of clay for balls is quite inadmissible.

These clay balls are connected with so many drawbacks, that something else was soon looked for. This was indispensable where nothing but smalls could be obtained, or where they could be procured so cheaply that acid-makers wished to dispense entirely or partially with using lump ore. At the pyrites-mines there were formerly enormous heaps of smalls, which were not saleable at all and would sometimes have been given away for nothing, just to make room. In other places pyrites only occurs in a loose, roughly crystalline shape; and, again, in others it is obtained by wet preparation altogether in the state of smalls. Thus there was great encouragement for constructing apparatus for burning small pyrites in large quantities.

The contrivances for burning pyrites-smalls may be divided into three classes, namely, those working by external heat, those utilizing the heat of ordinary burners for pyrites in lumps, and those arranged for burning the smalls by themselves without any extraneous apparatus.

(a) *Burning Pyrites-smalls in Coal-fired Furnaces.*

Apart from the use of "balls," the oldest plan of dealing with pyrites-smalls is that of spreading them on the bed of a furnace, heated by flues underneath, the fireplace being arranged at one end and the pyrites-dust being introduced at the other, and being gradually moved forward towards the fire end, as room is made for it by drawing out the burnt ore. In thus being turned over many times on its way from one end of the furnace to the other, the sulphur was supposed to be thoroughly burnt. This is, however, but imperfectly the case, even if the furnaces are made 100 feet long. Moreover, the cost of fuel in the best case is very heavy (at least 10 cwt. of coal is consumed for a ton of pyrites, usually much more), so is the cost of labour; the continuous opening of the working-doors causes very much false air to get into the chambers, even fire-gases sometimes leak through the furnace-bottom, and therefore the consumption of nitre and the yield of acid are very bad. We shall, consequently, not go into any details respecting these "muffle-furnaces," but refer to the first edition of this work, where, on pp. 186 to 190, the Belgian furnaces, and those of Spence, of Godin, of Imeary and Richardson, are described and partly illustrated by diagrams. Since it has been recognized that no extraneous heat is necessary for burning pyrites-smalls, such furnaces must be looked upon as altogether irrational, and they are practically obsolete now. This, of course, has nothing to do with the fact that similar furnaces are in use for roasting galena and other ores which do require external heat for the purpose.

(b) *Burning Pyrites-dust by the heat of Burners for Lumps.*

This was considered a great improvement upon the older methods, but it must be equally pronounced obsolete now, at all events in the case of ordinary pyrites. We shall therefore treat these processes very briefly, referring for details to the first edition of this work.

The first furnace for burning pyrites-smalls by means of the heat from lump-burners seems to have been that patented in France by Usiglio and Dony, Jan. 24, 1852, which, however, did very imperfect work. Much more important is the furnace constructed by Olivier and Perret, which was introduced into the majority of French works and was in use there for many years, until replaced by the Malétra burner (*vide* p. 334). Olivier and Perret placed above an ordinary lump-burner a number of shelves made of fire-clay, and charged with a thin layer (not above ¾ inch) of pyrites-dust (for exact description and diagrams, *vide* first edition of this work, pp. 193 to 196). In this way it is possible to burn about 1 cwt. of dust to each 2 cwt. of lumps, the sulphur in the cinders being reduced down to 4 or 5 per cent. The whole furnace was originally about 20 feet high, which necessitated a second working-stage above the ground. There is, of course, a good deal of labour connected with this system. Later on it was made lower, and so arranged that all the doors were on one side, so that a number of furnaces could be grouped into a set.

In a simpler form, namely, that of a single cast-iron plate above ordinary lump-burners, this system was introduced into some Tyneside works, first by MacCulloch, but was soon abandoned again (comp. 1st edition, pp. 191 to 193).

Another way of carrying out the same principle was the furnace of Hasenclever and Helbig (1st edition, pp. 196 to 201). Here, at the end of a set of lump-burners, a tower-like apparatus was arranged with eight inclined shelves of fire-clay, over which the dust was gradually to slide down and to be burnt on its way. Thus from 10 to 16 cwt. of smalls were to be burnt for each 48 cwt. of lumps; but the principle of automatic sliding down did not answer; the motion of the dust had to be aided by handwork, with much introduction of false air; and although a large number of these furnaces were erected, principally in Germany, they have been almost or entirely abandoned for some time past, and we abstain from describing them in this edition.

(c) *Burning Pyrites-smalls without external heat.*

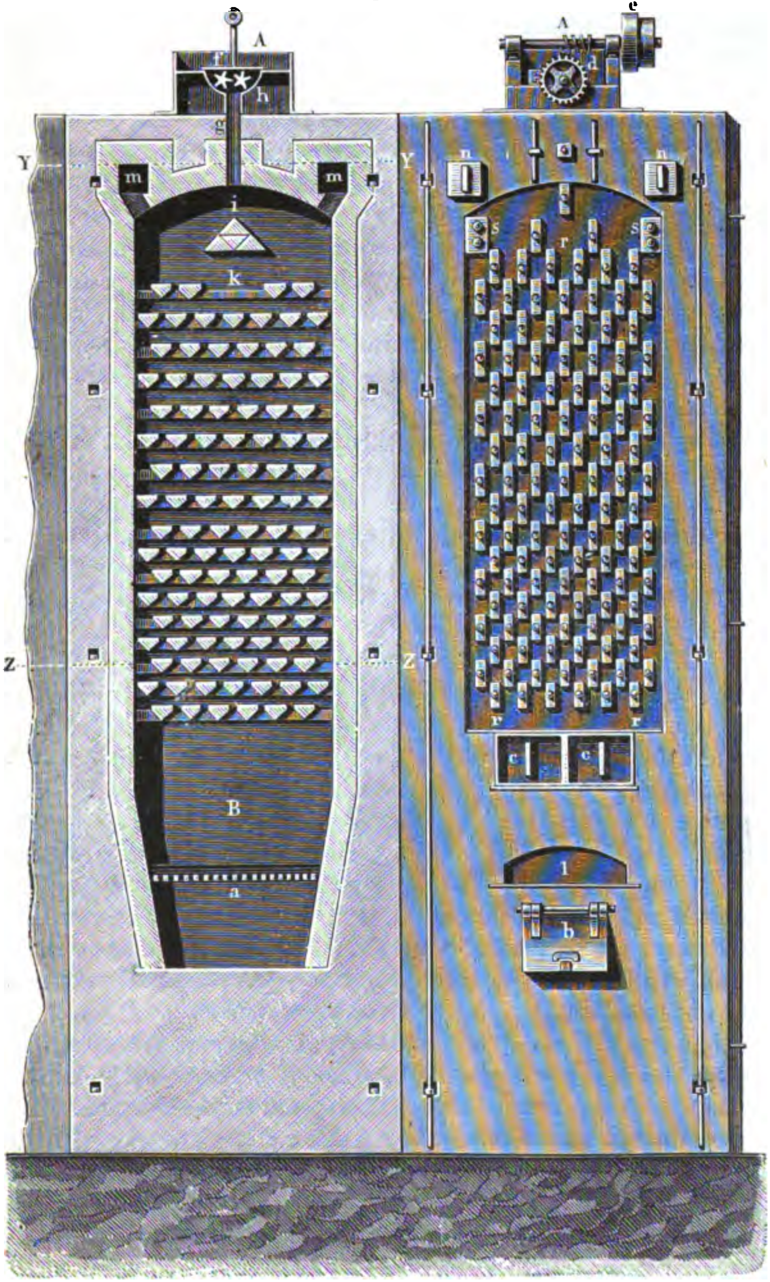
We must, in the first place, mention a plan which does without any special dust-burners, and only represents an improvement in making "balls." It is based upon the fact that pyrites, if it is in the shape of very fine powder mixed with water, coheres to a solid mass *without the aid of any plastic substance.* The fine pyrites-dust, in the presence of water and air, begins to oxidize very soon, even at the ordinary temperature; thus basic ferric sulphate is formed, which firmly cements together the separate grains of dust. This only takes place to a sufficient extent if the grains of dust are very fine and the mixture with water very perfect; and this can never be attained by merely sifting and moistening the fine ore. The ore must therefore be ground finely with water in a mill, for which purpose usually the so-called *pug-mills* are used, a kind of vertical mortar-mill, sometimes with revolving bottom dish, or, if the dish is stationary, with a mechanical arrangement for throwing out the mixture as soon as it has reached the proper consistency. The pyrites-smalls are thrown into the mill, water is run on, and the mill is run till a homogeneous mixture similar to fine mortar has been formed, which by itself has somewhat plastic properties. This mass is dried in layers of ½ inch thickness on the top of the pyrites-burners, often in cakes about 18 inches square; and after twenty-four or thirty-six hours it has hardened sufficiently for use. It is broken up into pieces of the same size as the lump ore, and charged along with this into ordinary pyrites-burners. In this it is not necessary to observe a certain proportion; for the balls made in this way are so hard that they can be thrown to the ground without being broken, they do not fall to powder in the burners, and burn out as well as lumps; their cinders are, of course, of the same value as those from lump ore, whilst those mixed with clay make the utilization of the ferric oxide, at last obtained at the copper-extraction works, very difficult.

The principal drawback of the process is this, that the mills suffer very much wear and tear from the hard pyrites. In spite of this, it was formerly the most usual in the large English works. The labour of grinding, carrying to the top of the burners for drying, taking down, breaking up, and laying down in front of the burners amounts to 1*s.* 4*d.* per ton. To this must be added 6*d.* for coals for working the mill, and wear and tear of the same, altogether about 2*s.*, apart from the wages for the burning itself (another 2*s.* per ton).

The same result as is attained by the "pugging" process is obtained in perhaps a more complete, but decidedly far more costly, way by the process of H. Wurtz (U.S. Pat. 252,287). He mixes the fine ore with powdered metallic iron, moistens this with a solution of sulphate of iron, and allows the whole to agglomerate by rusting.

The process just described is not applicable in cases where the great bulk or the whole of the pyrites employed is in the shape of dust. In such cases formerly the only available contrivance was the above-mentioned muffle-furnace, with all its great drawbacks. The first who proved that the heat generated by the combustion of ferrous bisulphide is sufficient for keeping the process going without any external aid, quite as well in the case of pyrites-smalls as in that of lumps, was Moritz Gerstenhöfer, whose furnace is described at length and shown in several diagrams in the first edition of this work, pp. 205 to 215. We here give only one diagram, fig. 89, and a short description. It consists of a shaft, 17 feet high, 2 feet 3 inches long, and 2 feet 7½ inches wide inside, provided with a large number of prismatic fire-clay bars, so disposed that the intervals of each upper tier are covered by the bars of the next lower tier. The pyrites-dust is fed in by means of fluted rollers, and drops from tier to tier, forcing down the particles

Fig. 89.



previously lying on the bars according to the natural slope of the ore. Before starting the feed of the ore, the furnace is brought to a bright-red heat by means of a coal-fire. Afterwards the combustion of the pyrites by means of the air entering from below is quite sufficient for keeping up the heat.

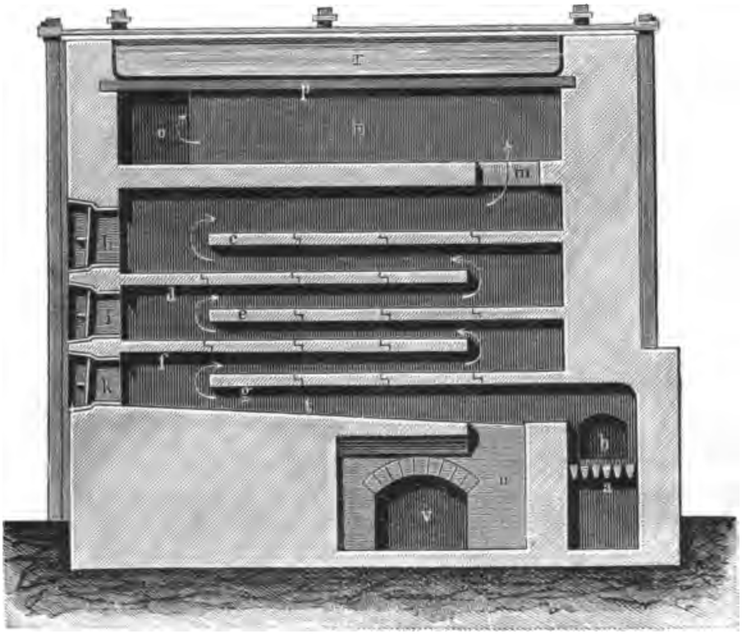
The two great drawbacks of the Gerstenhöfer burner are: the very large amount of flue-dust produced in it, and the very incomplete desulphurization of the ore (8 or 10 per cent. S in the cinders). Principally for these reasons this ingenious furnace has been abandoned again nearly everywhere, and is now only used for roasting "coarse metal" in a few copper-works. At the Freiberg works, where it was used for a variety of mixed ores (25 to 36 per cent. S), it has also been replaced by the Rhenania furnace, to be described below.

According to Scheurer-Kestner (Bull. Soc. Chem. xlv. p. 228), Perret later on constructed a furnace, resembling Gerstenhöfer's, but free from the defects of the latter. The pyrites was stated to be thoroughly utilized and the cost of labour reduced to one-half as against Malétra's "shelf-burners" (see below). At the time of Scheurer-Kestner's report the furnace in question was evidently still in the experimental stage; and as nothing more has been heard of it, its success cannot have been so great as anticipated.

The object but imperfectly attained by Gerstenhöfer's invention has been realized by a very simple plan—so simple, indeed, that it was not thought worth patenting at the time, although it has subsequently proved to be of immense importance. Mons. Malétra, owner of the works of Petit Quevilly, near Rouen, after having for some time burnt his smalls by means of an Olivier-Perret furnace, conceived the idea of separating the upper part of this furnace from the lower, and working the dust by its own heat of combustion without any aid from a lump-burner. This idea, which was worked out about 1867 with the aid of M. Tinel, proved entirely successful; but in spite of this, and also of the "*shelf-burner*" being the simplest and cheapest of all dust-burners, it became comparatively slowly known; but since 1873, when it became better known through the Vienna Exhibition, it has spread on the Continent with extraordinary rapidity, whilst for a long time it attracted little attention in England. The first burner out of France seems to have been erected at the works of Schnorf Brothers, at Uetikon, near Zürich, in 1870; in Germany the first was erected at Kunheim's works in Berlin. Even if, as it would seem, some form of these simple shelf-burners had been previously in use here and there, their *successful* application for burning pyrites-smalls seems first to have been effected by Malétra's works.

Fig. 90 gives a longitudinal, fig. 91 a cross section, the latter through two furnaces. Usually a whole set is built in a row. In order to start it, a coal-grate, *a*, and fire-door, *b*, are provided, which are walled up when the burner has got up to a white heat. During

Fig. 90.



this time the top working-door remains open. Then the five plates, *c*, *d*, *e*, *f*, *g* are charged with small ore through the doors *h*, *i*, *k*, whereupon the pyrites takes fire at once. The air enters through *l*, and is regulated at will. The gas travels over all the plates in a serpentine manner, indicated by the arrows, escapes through *m* into the dust-chamber, *n*, and through *o* into the acid-chamber or into another dust-chamber. The chamber *n* is covered by a metal plate, *p*, upon which lead pans, *r*, *r*, are placed, in which all the chamber-acid can be concentrated from 112° to 144° Tw. The acid of one pan communicates with that of another (as usual) by siphons or by simple run-overs. Each of the shelves, which are 8 feet long and 5 feet wide, consists of eight plates in two rows of four each; they rest, at the sides, in the walls of the burner, in the middle on fire-clay bearers, *s*, *s*, whose shape is better shown in fig. 92. They are not equidistant, as can be seen in the drawing; the upper shelves, where more gas is evolved, are wider apart than the lower ones, where the radiant heat of the shelves is all the more useful. The best distance for the upper shelves is 4½ inches. In order to burn a larger quantity of pyrites, it is not possible to leave the ore lying quietly, as in Olivier-Perret's burner: since here the external heating by the lump ore is missing, the combustion would be too incomplete, and the heat would soon get so low that the burning would cease. The mass must therefore be moved, which is done in the following way:—Every four hours the contents of the lowest plate, *g*, are

Fig. 91.

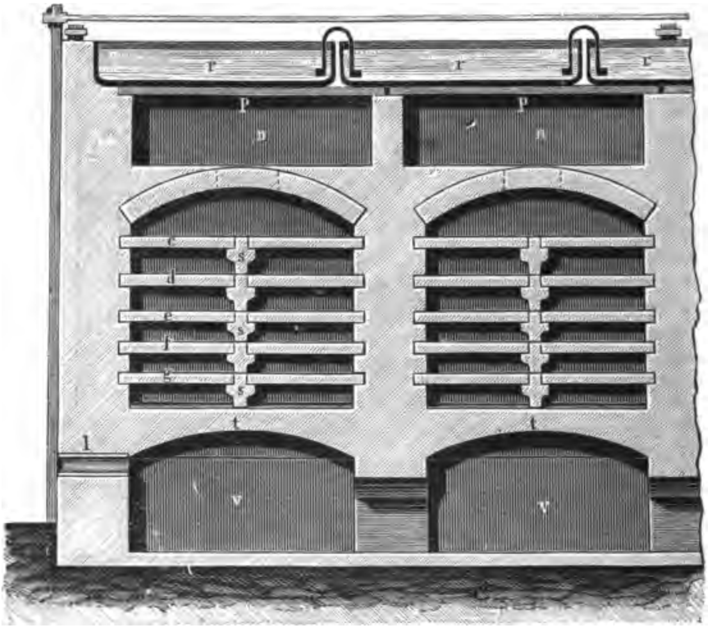
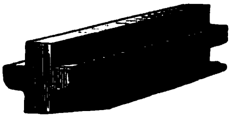


Fig. 92.



drawn through the door *k* on to the arch *t* (which is level at the top, but slopes behind), after the burnt ore lying on the arch has first been pushed through the door *k* to the opening into the pit *u*. Then through the door *i* the contents of *f* are pushed down to the plate *g*, and there levelled again. Thus the higher plates are successively treated, till the highest plate, *c*, is emptied and can be charged with fresh ore. If four furnaces go together, one of them is on turn every hour. The contents of the pit *u* are removed once a day by the door *v*. The movement of the ore by removal from one shelf to another causes its thorough combustion, and thus also raises the heat. Four furnaces of the above dimensions burn daily 3 tons of pyrites. From 6½ to 7 lbs. of ore are calculated for each superficial foot of shelving.

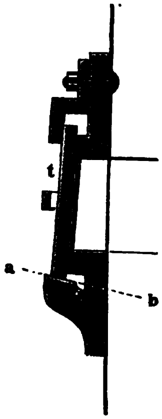
Sometimes the shelves are made in the shape of a very flat arch, for the sake of greater stability; or at least the bottom is arched, especially in the case of wide shelves. Some prefer building the furnaces in such manner that the fire-clay slabs forming the shelves are nowhere enclosed within the brickwork of the walls; they are then more easily replaced when broken.

The Malétra burners have recently been improved by making the fire-clay shelves stronger and doing away with the middle bearers, *s*, *s* (fig. 92), which give much trouble in working the burner. These single shelves are made from 3 feet 3 inches to 3 feet 7 inches inside.

Malétra's burner, which has obtained general acceptance in Germany, has been improved there by Schaffner, P. W. Hofmann, Bode, and others.

Through the kindness of Dr. Max Schaffner, of Aussig, I was enabled to obtain detailed drawings of the shelf-burners as modified by him, and these are reproduced and described in our second edition, pp. 255 & 256. This furnace has seven plates, each served through its own door—three on one side, four on the other. On the first side there is also the ash-pit door, 18 inches square, for drawing out the cinders, which is thus done in the usual way, not by the rather inaccessible pit of Malétra. The doors all slide with their planed margins on equally planed ledges cast on the front plates, so that luting or plastering is not necessary. A certain number of angle-pieces are bolted to the front plates; these, between their outer bend and the planed ledges, leave sufficient room for the doors *t* to slide each way on the inclined face *a b*; and there is a sufficient number of such pieces present for each door to be always held by three of them (fig. 93). This style of work is evidently much cheaper than casting everything in one piece, because the planing is much easier; it is also cheaper than the English style, shown on pp. 298 and 299, and quite as substantial as the latter. There are no special openings for the air, as, in spite of the planed surfaces, sufficient air enters to support the combustion. The regulation of the draught is here effected entirely by the chimney-damper.

Fig. 93.



In this burner *dust and peas* are burnt *together*, and the sulphur is burnt down to 1 per cent.; thus the grinding of the smalls, which is still practiced at some works, is done away with.

The Aussig or Schaffner dust-burner has been erected in many works from the plans given in the previous edition of this book, and that with entire success. Of course at some places minor modifications have been introduced, but the principle is always the same, also in the plans given by Falding in 'Min. Ind.' vii. p. 668.

Most manufacturers now consider that burners worked from both sides allow too much false air to enter, and therefore prefer arranging two rows back to back. I am enabled to give full drawings of the most modern dust-burners from the designs of Mr. H. H. Niedenführ, as shown in figs. 94 to 96. They are clear enough to require no further description.

According to communications from Mr. Benker, he still (1902) builds his Malétra furnaces on the old system (p. 335), all the compartments in one line. On the top he places a collecting-flue and dust-chamber, 5 feet high; at the end of the set a large dust-chamber, of the same height and width as the furnace and 20 to 30 feet long, according to the description of ore. One man serves two compartments. Each of these burns 20 to 24 cwt. of 50 per cent. pyrites per 24 hours, but up to 32 cwt. of poor ore, such as he had to work in Italy, containing 26 per cent. sulphur and 3 per cent. copper, of which 90 per cent. was soluble in water and 95 per cent. soluble in dilute sulphuric acid after roasting.

The ore is spread on the plates by means of a tooth-rake, producing an undulated surface and not leaving any bare places. From such poor ores Benker obtained gases with 7·7 per cent. SO_2 on the average, and produced 6·2 kg. acid of 106° Tw. per cubic metre (=0·39 lb. per cubic foot) in 24 hours, with a consumption of 0·7 parts nitric acid 66° Tw. to 100 sulphuric acid 106° Tw.

One of the principal advantages of the shelf-burners is that the ore is burnt out to a much larger extent not merely than with any of the older forms of dust-burners, but even with the best lump-burners. Even without grinding the smalls, it is quite easy to keep the sulphur in the cinders down to 1·5 per cent. At many works, *e.g.* at Uetikon, the average amount of sulphur in the cinders never exceeds 1 per cent., and frequently it is below. At Malétra's own works they get down to 0·6 or 0·8 per cent., but this can be done only by crushing the smalls down to an almost uniform fine powder. The amount passed through the burner also influences this. Sorel states that a set of burners, charged with 34 or 35 kils. of ore per square metre every 24 hours, was regularly burnt down to 0·75 per cent.; with 36 kils. the sulphur in the cinders rose to 1 per cent., with 32 kils. it fell as low as 0·42 per cent. Jurisch, in his 'Schwefelsäurefabrikation' (p. 80), quotes 30 kils. pyrites per square metre of plates, with variations from 25·6 to 35·8 kils. Stolzenwald (Chem. Zeit. 1901, p. 22), when burning Hungarian pyrites (47 per cent. S), was not able to burn more than 24 kils. per square metre of Malétra plates, in order to get down to 1·7 per cent. S in the cinders.

I have seen in Germany shelf-burners working up "peas" of Spanish ore down to 2·8 per cent. S, and even real "lumps" of Westphalian ore down to 3·5 per cent. S.

Such results can, of course, only be obtained with pure ores, free from zinc, lead, &c. Hence the cinders from shelf-burners are readily bought by iron-works, both for blast-furnaces and other purposes.

In a six-shelf burner there ought to be scarcely any purple flame visible when pulling the charge down from the top shelf to the second shelf. The second shelf is at a bright red heat, the third one less so, and so forth; the back part of the fifth ought to be visible only at night by the light radiated downwards from the fourth, and the sixth ought to be perfectly black. Krutwig and Dumoncourt (Chem. Zeit. Rep. 1898, p. 242) found the temperature on the top shelf=680°, on the second 750°, on the third 720°, on the fourth 650° C.

Sorel found the following percentages of sulphur on the different shelves :—

Sulphur in green ore.........	50 per cent.
First shelf	32 ,,
Second ,, ...	17 ,,
Third ,, ...	7 ,,
Fourth ,, ...	5 ,,
Fifth ,, ...	2 ,,
Sixth ,, ...	0·75 ,,

He regularly detected half of the sulphur in the cinders in the shape of FeS, the other half in that of sulphate.

Crowder (J. Soc. Chem. Ind. 1891, p. 298), in working with shelf-burners containing seven beds, charged once every eight hours (so that the charge takes 7 × 8 = 56 hours to complete the course), found the following percentages of sulphur on the different shelves (nearly agreeing with Sorel's results mentioned in the text) :—

	Average of 23 trials.	Ditto of 26 trials.	
Ore charged	50	50	per cent. S.
No. 1 shelf	32·27	32·81	,,
2 ,, ...	21·41	17·55	,,
3 ,, ...	12·77	11·09	,,
4 ,, ...	6·39	5·05	,,
5 ,, ...	4·08	3·42	,,
6 ,, ...	2·35	2·56	,,
7 ,, ...	2·27	1·96	,,

If there is too much draught, the lower shelves cool down and the upper ones get hotter. This may cause the process to appear as going on very well; but it soon turns out bad. If, on the contrary, there is too little air, the bottom shelf becomes luminous and the sulphur in the cinders rises rapidly. In both cases there is incipient fusion on the second shelf, which prevents the roasting from being carried through. This can be remedied by admitting a little air at the door of the second shelf, or even mixing a little dead ore with the charge. The admission of air to the intermediate shelves serves also for bringing forward any burners which have got behind, and to burn any sulphur subliming from the first shelf, in case the burners are going too hot, or from damp pyrites giving off sulphuretted hydrogen; but this expedient, useful as it is when properly handled, must be employed with caution lest the bottom shelves get too cold from want of air.

In the normal style of working all the air required for converting the sulphur into sulphuric acid enters at the bottom shelf, and this large quantity of cold air may lower the temperature of the nearly burnt-out mass to such an extent that no more ferric sulphate is decomposed. It was at first sought at Malétra's works to avoid this by leading the burner-gas downwards underneath the bottom shelf, thus heating the latter and employing the ground-space as a dust-chamber; but this plan did not answer and was soon given up again. It has even been tried to utilize the heat of the burner-gases for a previous heating of the air serving for the burning-process. But evidently this must most seriously interfere with the draught, and will hardly answer in the long run. The same advantage could be secured more easily by admitting at the bottom only the quantity of air absolutely necessary for completing the roasting of the air, and allowing the remaining air to enter by a regulating-slide in the top working-door. In this case the bottom shelf will be visibly red-hot in the dark. This plan can be carried out only where the draught is very good, for instance by making the gas to rise to a considerable height before entering the chambers, and never leading it downwards in any part of its course. The burner walls should in this case be made thick or hollow to prevent loss of heat in the lower part; on the contrary, an overheating of the top shelf should be avoided by making the gas-flue rather high and causing the heat to be dissipated there, most rationally by means of evaporating-pans for sulphuric acid. Another plan is, introducing the requisite excess of air into the first chambers by means of an injector.

The shelf-burner answers best for rich ores. With 50 per cent. ore good results are obtained when burning from 32 to 37 kils. of pyrites per superficial metre (= 6·5 to 7·5 lbs. per square foot) in 24 hours. One may go down to 28 kils. (=5·7 lbs.), but only exceptionally, because the burners cool down too much.

For poor ores, say below 38 per cent. of sulphur, the shelf-burner does not answer.

The management of shelf-burners is really easier than that of lump-burners, but it involves a little more labour. It is generally assumed that one man can charge, burn, and withdraw a ton of pyrites every day; but it is possible to get up to 25 cwt. It seems best to give five burners to each man, so that each burner is charged every five hours. The phenomenon of scarring is hardly ever noticed here. The working-doors must never be left open any longer than is absolutely necessary for the work; in this case both the yield of acid and the consumption of nitre are just as favourable when working dust on a shelf-burner as with the best lump-burners. This is the uniform testimony of the many works I have visited.

In order to start a new burner (which, of course, must have been thoroughly dried first in the ordinary manner), the communication with the chambers is stopped and a fire is lighted on the shelves, beginning with the bottom, sometimes by means of a temporary chimney. After four or five days, when the burner is moderately red-hot (it is unnecessary and even injurious to get it up to a *bright* red heat), the remainder of the fuel is cleared away, pyrites is charged on the three top shelves, and communication so made with the chambers, whereupon the regular service is started as previously described.

During the last twenty years the shelf-burners have also been introduced into a number of English works, and everywhere with great success. This has been done on the largest scale at the Newcastle Chemical Works (Allhusen's), where 129 shelf-burners on Schaffner's plan, described in this book, have been erected, which consume from 600 to 650 tons of pyrites-smalls (Mason and Barry's) per week. Each burner is charged, once in 8 hours, with from 4½ to 4¾ cwt. of smalls.

The objections made to the shelf-burner in its employment for sulphite paper-works by Harpf have been refuted by the author in Zsch. angew. Ch. 1896, pp. 65 & 157.

Combination of lump-burners and dust-burners for the same set of chambers.—Such a combination is generally avoided, as the conditions of draught are very different in each case. I have, however, seen a combination of the above-mentioned kind in excellent operation at the Stassfurt potash-works managed by

Dr. Bernhardi, the good result being brought about by placing the shelf-burners so low that the top shelf is on a level with the charging-door of the lump-burners. This causes an upward draught in the shelf-burners, and prevents their blowing out, even when the doors are opened.

Other Descriptions of Shelf-burners.

The furnace of Finch and W., J., & S. Willoughby (E. P. 2913, of 1883) differs from a Malétra burner only in that the shelves, instead of being placed horizontally, are inclined alternately in opposite directions.

A modification of the Malétra burner has been patented by Mactear (no. 3701, 1878).

A furnace, combining some of the features of the Gerstenhöfer and the Malétra burners, has been patented by Hasenclever and Helbig (description and diagrams, 1st edition of this work, pp. 220 to 222). It has never been carried out in practice, and is not likely to be so now.

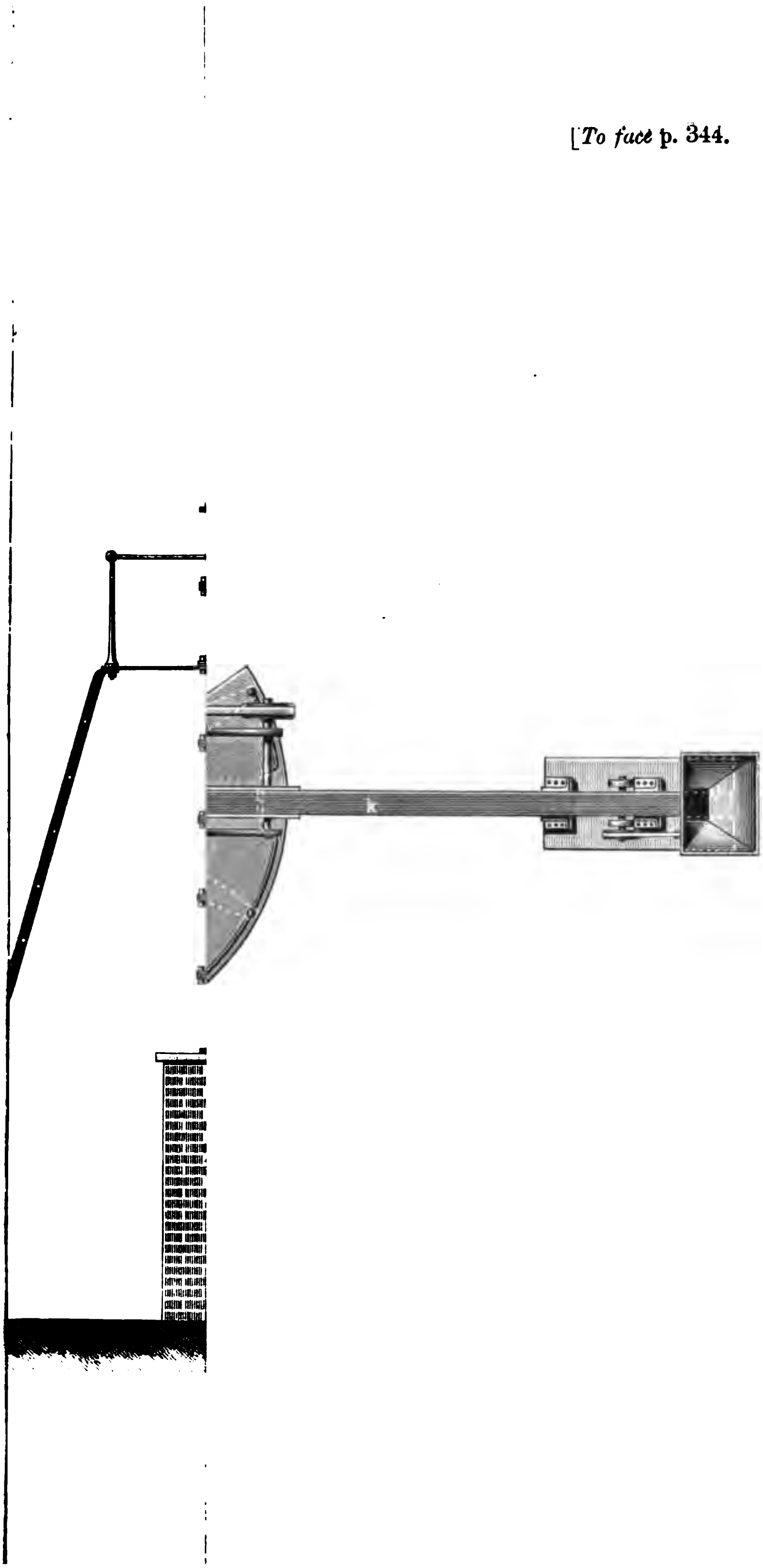
E. Bramwell (G. P. no. 22,758) has constructed a somewhat complicated pyrites-burner, in which, contrary to the ordinary dust-burners, the fresh air meets with the green ore, the products of combustion being gradually led over partially roasted ore, and at last over the almost spent cinders. This is effected by placing five calcining-beds in a row, each of them provided with an outlet for the gas connected with a gas-main, to be connected or disconnected by means of a throttle-valve, so that the current of gases can be directed at will. The last burner of the series communicates with the first by means of a flue underneath, so that a regular rotation can be kept up, as is done in lixiviating vats for black-ash.

Mechanical Dust-burners.

The necessity of frequently opening the doors in Malétra's and all similar furnaces is certainly a drawback; it necessitates much labour and cannot but introduce some false air. These drawbacks have been overcome in a most ingenious way in the mechanical pyrites-dust burner constructed by MacDougall Brothers, of Liverpool; but unfortunately fresh troubles have arisen there which have caused these burners to be abandoned again. Still, as in theory they are the most perfect of all dust-burners, we will describe them here, especially since the drawbacks connected with them have been overcome by later inventions. The MacDougall burner is shown in figs. 97 to 99.

The burner consists of a metal cylinder, 6 feet in diameter and 12 feet high, formed of seven rings (*aa*) bolted together, and provided with a solid bottom, but open at the top. The rings are cast in such a way that the lower and inner edge of each can serve as an abutment for one of the flat arches b_1 to b_6, which divide the inner space of the cylinder into seven chambers, the uppermost of which is open at the top. The arches, as well as the cast-metal bottom of the cylinder, are pierced in the centre, and allow the passage of a cast-iron shaft, *c*, 6 inches thick, which is turned by means of the toothed wheel *d*, the pulley *e*, and the steam-engine *f*. The shaft carries at top and bottom the lutes *g* and g_1, into which the cups *h* and h_1, fixed to the top arch and the cylinder-bottom, enter; the latter are fast, whilst the lutes *g* and g_1 turn round with the shaft, and a hydraulic joint prevents the escape of gas at the places where the shaft enters and leaves the cylinder. To the shaft are fixed the cast-iron arms, i_1, i_2 . . . i_7, provided with teeth along their lower margin. The teeth are placed alternately in opposite directions; so that the arm i_1 moves the ore-dust from the centre to the periphery, i_2 the same from the periphery to the centre; i_3 acts like i_1; i_4 like i_2, and so forth. Corresponding to this, the arches are perforated alternately—b_1, b_3, and b_5 near the margin, b_2, b_4, and b_6 in the centre. The latter have a large central opening, 1 foot 3 inches wide, lined with a metal pipe, which gives free play round the shaft to the gas and the ore-dust; whilst in the other arches the shaft is so tightly surrounded by a metal pipe that scarcely any dust, and still less gas, can get through. The small ore (which need only be passed through a 1-inch riddle, and therefore contains pieces up to the size of a walnut) is lifted by the elevator *k* (also moved by the engine *f*), and is emptied on to the top flat, b_1, where the arm i_1 takes it round and gradually moves it towards the periphery. During this time the ore is completely dried by the heat of the gas below. The ore dropping down the edge at *l* from the open top chamber is continually pushed into the first closed chamber by a ram at A. The ram A can be moved reciprocally either by the rod B

[*To face* p. 344.



or C, and can be moved more or less quickly ; so that the feed of ore can be regulated to a nicety. The arm i_2 moves the ore towards the centre of b_2, where it drops down ; i_3 moves it towards the periphery of b_3, where it drops down again, and thus quite gradually and constantly, being directed by the teeth of the arms, arrives at the bottom, and is emptied out through the pipe *m*. The two slides, *n* and *o*, allow the contents of *m* to be got out without any loss of gas or any air entering the other way. As the furnace during the operation is in full heat, most of all near the top, the ore ignites as soon as it arrives on the bottom of the first closed chamber, b_2 ; and in its gradual zigzag way towards the bottom the sulphur is completely burnt off. The air is continually supplied by the air-pump *p* in exactly the necessary quantity; and the gas escapes through the pipe *r* to the acid-chambers.

An apparatus such as is here figured is sufficient for burning 3½ tons of ore in 24 hours ; with eight closed chambers instead of six, it can burn 5 tons. It is also very well adapted for burning the spent oxides of gas-works; but then it must have only four chambers. In a factory on the Tyne, where this apparatus was at work for a while, the consumption of coals for driving the engine amounted to 4 tons per week. A two-horse-power engine and a 1½-inch steam-pipe are said to suffice for the largest burner. The wages amounted to £4 5*s*. per week; but this rather high amount was explained by the fact that two other furnaces were building, which were expected to be served by the same men who attended the first. Of course this apparatus is quite independent of the skill of the burner-men, which is mostly acquired only after some years' practice.

For heating up, the engine is started and the cold furnace is gradually filled, care being taken to regulate the thickness of the layers of ore on the different floors. When the ore has arrived at the bottom, the engine is stopped, and the flame of a temporary fireplace, built against the cylinder, is allowed to enter it, until the ore lying on the bottom and the floor b_2 has taken fire. Then the engine is started, the temporary fireplace is taken away, the man-hole is closed, and nothing remains but to see that the ore arrives at the bottom properly burnt. If this should not be the case, the speed of the feeding-ram A, that of the air-pump, or that of the agitating-shaft is altered till everything is in order. It is easy to get the sulphur in the burnt ore down to 1 per cent.; in forced work only 3 to 4 per cent. can be attained.

One objection will at once be made to MacDougall's burner, viz. that the machinery in its interior must wear out very quickly. In order to obviate this, all parts of the machinery are made of thick cast-iron; and when one of the arms is worn out it can be renewed through the man-holes, *s*, *s*, without allowing the apparatus to cool down. That otherwise this burner has many very great advantages over all others is evident. The turning of the small ore is perfect without any opening of the doors and working by hand. Not even during charging and discharging does false air enter the burner; and by means of the air-pump exactly the necessary quantity of air can be admitted (this, however, in practice was found to be very difficult). This work, indeed, is done under such favourable conditions as are realized by no other burner, whether for pieces or for smalls; and it might be assumed that the consumption of nitre would thus be reduced to a minimum, and the yield of acid raised to a maximum. Nevertheless MacDougall's burner had to be given up again in the above-mentioned factory, because the quantity of flue-dust was so great that it could not be managed in any way, and the chamber-process was seriously interfered with. Employment of the Glover tower was not to be thought of. It does not appear that really efficient dust-chambers were employed. The air-pump acted so violently that the dust was carried away a great distance *. Probably this drawback might have been counteracted by some alteration in the construction; but, altogether, the machinery caused endless trouble, continually requiring repairs, and there is no doubt that it would have to be altered a good deal before it could become a real success.

The drawbacks ascribed to MacDougall's furnace were sought to be obviated by a new patent of the same inventor, E. P. no. 3985, of 1883. Dust-chambers are provided with perforated baffle-plates for the interception of dust carried over by the draught, arrangements being made for drawing out the settled dust without allowing gas to escape or air to enter. The shaft and rake-arms are constructed of cast-iron, having a central wrought-iron tube so as to obviate warping or bending from the effect of heat; and in order that the shaft may be readily withdrawn, the arms or rakes are

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* Davis ('Chemical Engineering,' ii. p. 120) mentions that with mechanical draught out of 25 tons of dust burned per week 4 tons were carried away as flue-dust!

fixed thereto by a fork-shaped end and cotter. A second modification is described, which is to avoid the dust occasioned by the vertical passage from floor to floor. The furnace is constructed of an oblong, horizontal floor or chamber, provided with a series of vertical shafts, having rakes similar to those above described and revolving in opposite directions. The teeth are so placed as to draw the material towards each shaft, and thus pass it from one to the other and from end to end of the furnace. Where prolonged roasting or burning is requisite, a similar furnace, or the first modification, may be superposed above the last mentioned, the material being first passed through the upper furnace.

A further improvement was patented by the same inventor as E. P. no. 22,504, 1891. Here the central shaft is made in several lengths, coupled together by widening one end of the shaft to form a square socket, and fitting into this the square end of the other shaft, the two being secured by a square key wedged between socket and square end; a tight-fitting spring-clip protects the coupling from the action of the burner-gas. The furnace-rings are joined together by half check-joints secured by set pans and rust jointing; the ends of the pins are not exposed to the corrosive fumes.

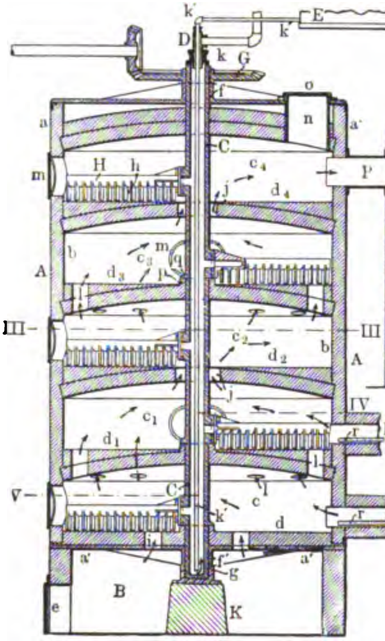
The subject of mechanical furnaces generally has been treated in detail by Bode, Dingler's Journal, ccxix. p. 55, and Wagner's Jahresb. 1876, p. 296.

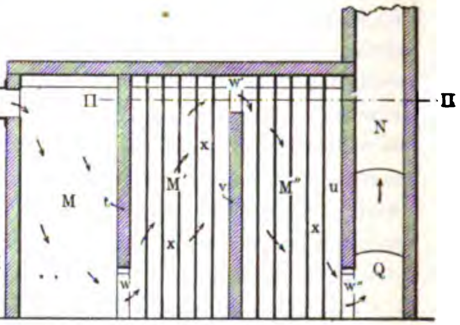
A furnace very much like MacDougall's was patented by Mr. Perret in France, on June 23rd, 1875.

A mechanical pyrites-kiln, greatly resembling MacDougall's in principle, has been patented by R. Mackenzie (E. P. no. 4418, 1881). It is provided with a water-cistern at the bottom, in the hope of promoting the process by the presence of aqueous vapour. Also a similar furnace, differing only in details of construction, has been patented by Black & Larkin (E. P. no. 4456, of 1881), and another by Johnson in America.

A much more important modification is the burner constructed by Herman Frasch, which avoids most of the difficulties of the above system by the introduction of water-cooling. The Frasch burner has been described by me in Zsch. f. angew. Ch. 1894, p. 15, from which parts of the drawings are reproduced here as figs. 100, 101, 102. We notice the hollow shaft C, 8 inches outside diameter, 5 in. bore. Above the cylindrical burner it is connected with the fixed water-pipe D by means of a stuffing-box. As we

Fig. 100.





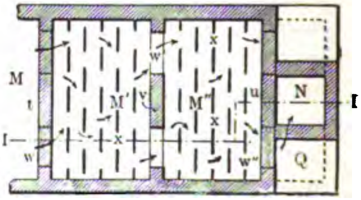
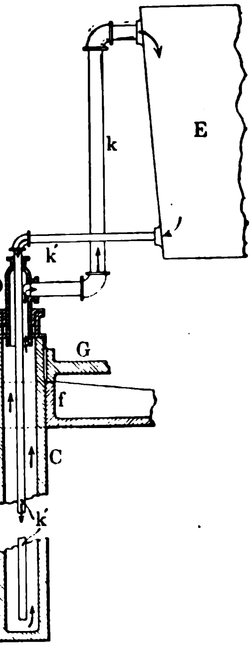


Fig. 101.

see from fig. 102, pipe *k* takes the water from the cistern E to the top of D, and pipe *k'*, starting from the bottom of E, reaches nearly to the bottom of shaft C. This causes a continuous circulation of water from E through *k'* downwards, then upwards in the annular space between *k'* and C, and back through *k* to E. Branch water-pipes reaching from C into the hollow stirrers H protect these also from fusing or deformation. Shaft C is, moreover, protected on the outside by wire gauze, covered with a paste of fireclay. The remainder of the figure can be easily understood by reference to the MacDougall

Fig. 102.



furnace, but attention must be drawn to the very efficient dust-chamber shown in sectional elevation fig. 100, and sectional plan fig. 101.

I have convinced myself by personal observation of the excellent function of this apparatus, especially also of the fact that the protective-water circulation between the hollow shaft C and the hollow side-arms H is quite sufficiently effected by the steam formed in the latter.

According to a report received from Mr. Frasch in 1902, his furnaces, which are now regularly made 16 feet wide, have done perfect work ever since; thirty of them are in operation at eight different works of the Standard Oil Company for the purpose of roasting metallic sulphides. The heat produced in the interior of the shaft and arms is utilized by attaching a steam-drum to the highest portion of the water circulation, and the steam is used under two atmospheres' pressure for distilling benzine out of light petroleum oils.

Another modification of the MacDougall burner is the Herreshoff burner, where the cooling is performed by air (figs. 103 & 104). This principle had been carried out exactly in the same manner already before 1883 by the blende-furnace of the Société Vieille Montagne (*vide infrà*, p. 364). This burner and its working are described in 'Mineral Industry,' vi. p. 236, and by Gilchrist (Journ. Soc. Chem. Ind. 1899, p. 460). The central shaft *a*, fig. 103, is hollow, 14 inches outside diameter and about ¾ inch thickness of metal. Above every shelf there is a cross channel or socket passing directly through the shaft, about 4 inches wide and 5 inches high. Into this socket the side-arms are inserted. In the top of the channel, at the centre of the vertical shaft, is a pocket running across the channel; into this a rib at the inner and top edge of the arm locks, when the arm is forced into its proper position, and the weight of the arm keeps it locked in the channel. By raising the outer end of the arm about 3 inches, the top edge of the rib is brought below the pocket and the arm can be pulled out. Each arm, weighing about 100 lbs., can be unlocked and removed and a new one inserted in about one minute. The greatest strain is at the point of contact with the central shaft; but the cooling effect of the air in the shaft prevents any damage, as the temperature never exceeds a dark red heat. About six of these arms, at a cost of less than £1 each, cover the renewals per annum. The arms are hollow,

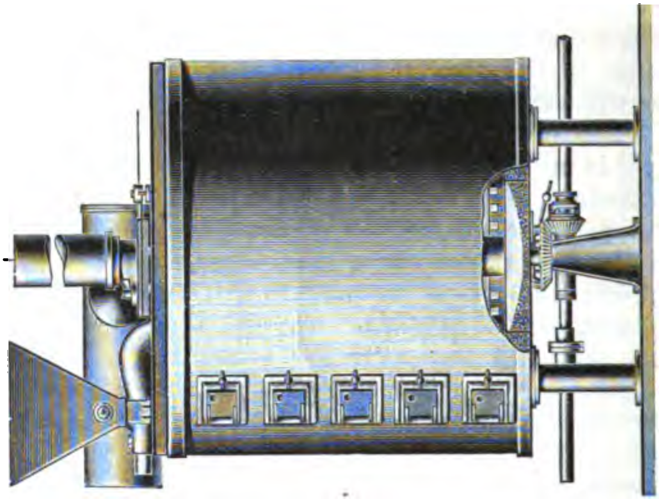


Fig. 104.

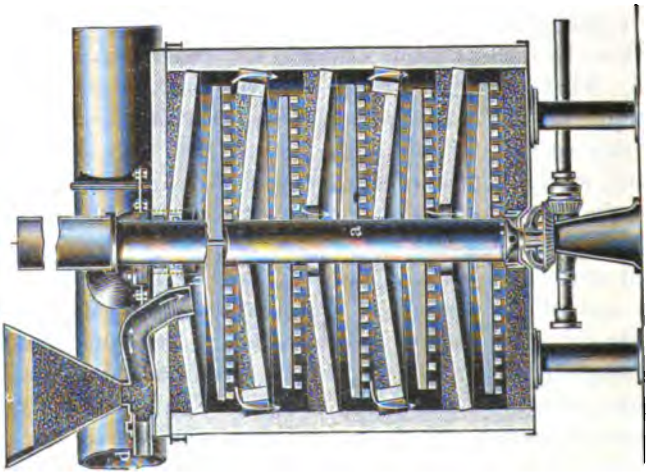


Fig. 103.

of a rectangular section, and are made of cast-iron capable of resisting the heat.

The cross channels do not take up the whole area of the shaft, but allow the air entering at the bottom to pass up the shaft; a light steel stack, about 10 feet high, provides the draught.

The five shelves are fire-brick arches, 4½ inches deep, levelled off with ashes or similar materials. The ore is fed automatically from the hopper *c* by means of the plunger *d* moving backwards and forwards. The passage down the shelves takes place exactly as in the MacDougall furnace. The central shaft revolves once in two minutes, the plunger makes one stroke per minute. There are two outlets for the burnt ore at the bottom, 5 × 3 inches.

The furnace is about 10 feet wide and 10 feet high. The outer casing is of ¼-inch steel, riveted together, with a red brick lining, 8 inches thick. The total weight is about 7 tons; the heaviest piece weighs a ton. The motive power is practically ⅔ H.P. per furnace. Each furnace roasts 6000 lbs. of 44 per cent. Virginia ore, or 49 per cent. Tharsis ore, in 24 hours. The amount of sulphur left in the cinders depends upon the quality of the ore, may be 2 or 3 per cent., or down to 1 or 1½ per cent. The furnace takes also low-grade ore, with 30 or even 25½ per cent. of sulphur. With magnetic pyrites (pyrrhotite) the grain should not be larger than wheat, with proper pyrites it may run from pea-size down to dust. When some sulphur is to be left in for the wet copper extraction process, up to 8700 lbs. per 24 hours can be treated. Spent oxide of gas-works can be also worked, but it is best mixed with pyrites fines.

At one American works where 70 of these furnaces are in operation only two men attend to them. A prospectus issued in November 1901 enumerates ten American and fourteen German, French, Austrian, and Italian factories where these furnaces were introduced ; four furnaces had been ordered by British manufacturers. During 1902 I heard great complaints about the unmanageable quantity of dust produced by these burners (comp. p. 346)

A. P. O'Brien has further improved the Herreshoff furnace (comp. Falding, Min. Ind. ix. p. 623), but no details or definite results can as yet be stated. Utley Wedge (U.S. P. 649,183 and 654,335) describes a similar furnace.

Other mechanical dust-burners.—Farmer and Hardwick's mechanical pyrites-burner (1878) resembles to some extent Jones's and Walsh's mechanical salt-cake furnace. It is automatically charged and emptied; 5½ tons of pyrites are said to be burnt off in from 7 to 9 hours. None of these furnaces seem to be in practical operation.

The mechanical pyrites-burner of P. Spence (patented in England Dec. 24, 1878; in Germany No. 9267; in America No. 248,521) is a shelf-burner provided with mechanical stirring arrangement. As this furnace seems to be constructed on rational principles, and as it has met with practical success in America, we give here a complete description of it.

Fig. 105 shows an exterior side view; fig. 106 a plan; fig. 107 a cross section of one half of a double furnace, the other half being shown in outside view; fig. 108 a longitudinal section of the furnace-beds; and figs. 109, 110, and 111 views of the stirring and raking instruments. The construction of the furnace-beds is best seen from fig. 108. In this there are at 1 the walls of the furnace, in which are fixed projecting fire-clay slabs, 2. Upon these are placed tiles, 3, reaching from one side of the furnace to the other, a number of these composing the length of each furnace-bed. In figs. 107 and 108 the several beds are shown at 3, 3*a*, 3*b*, 3*c*; alternate openings in these beds being shown at 4, 5, 6, 7. The pulverulent material is thrown at H on to the floor 3; advancing rakes or ploughs stir it and carry forward a portion of it through the opening 4 on to the second bed 3*a*. The teeth of the rakes are formed of a triangular section, as shown in fig. 111, the apex of the triangle being in the direction of the motion of each rake longitudinally from end to end of the furnace, the flat sides of the teeth of the rake being in the direction in which it is desired to traverse the ore along the bed of the furnace. When the rake is advancing in the direction of the pointed part of the teeth of the rake, the ore will be only turned over; but when the rake is moving in an opposite direction, a certain quantity of the ore will be carried by the flat side of the teeth along the floor of the furnace. Thus the ground material, delivered to the floor 3 at the point H, is stirred and subsequently partially carried forward till it is delivered through opening 4 on to the second bed, 3*a*, where the same operations take place, the material now passing down the opening 5 on to the bed 3*b*, and so through all the beds, until it is at last discharged through the opening 7 into the receptacle 8. Since the openings in the successive beds are on alternate ends of the furnace,

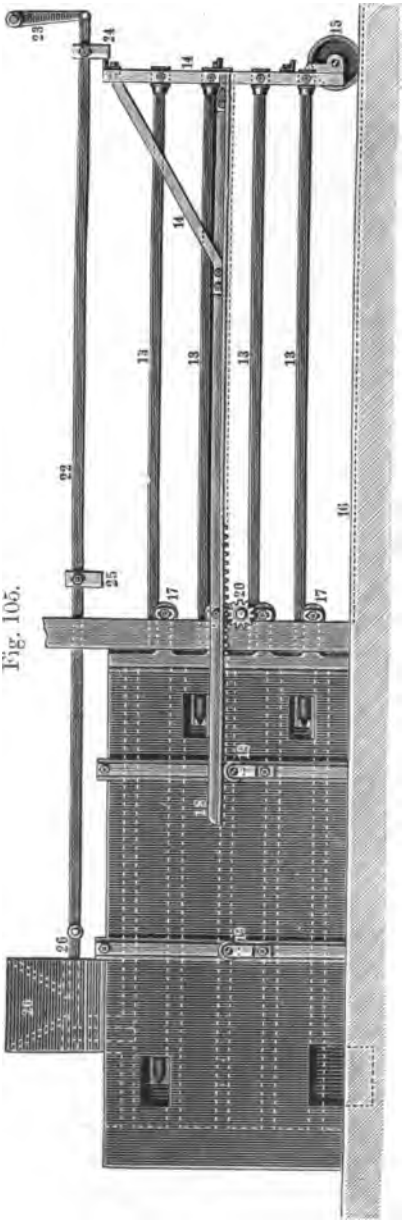


Fig. 105.

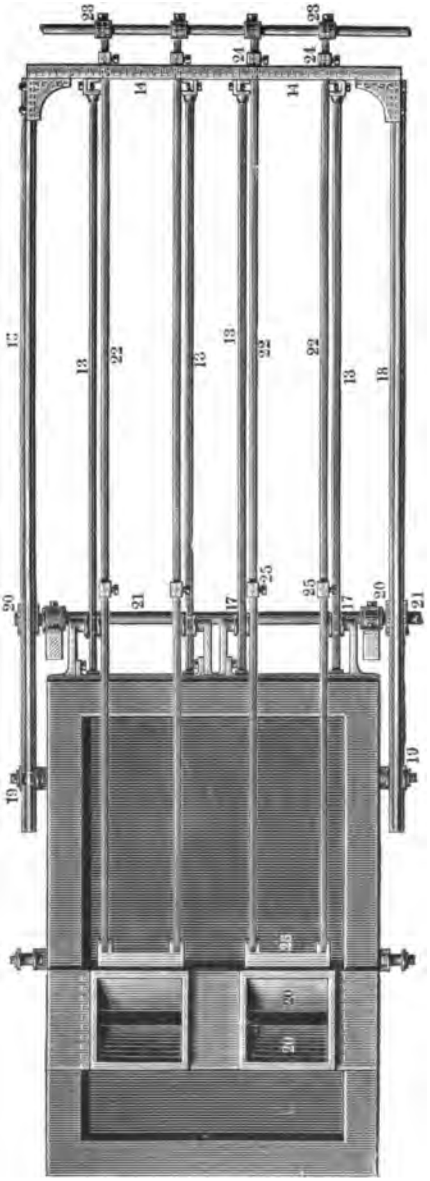


Fig. 106.

Fig. 107.

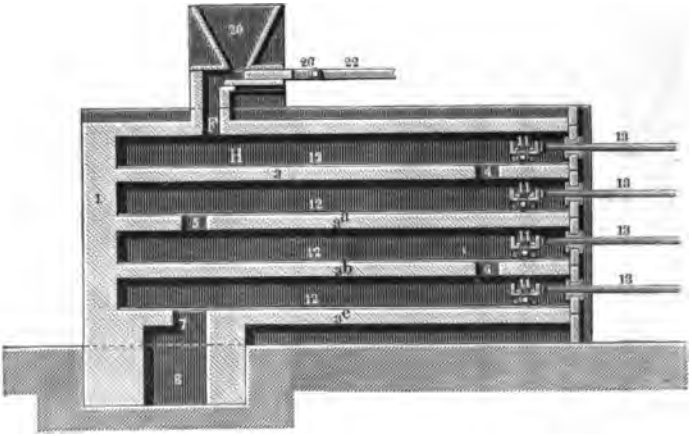


Fig. 108.

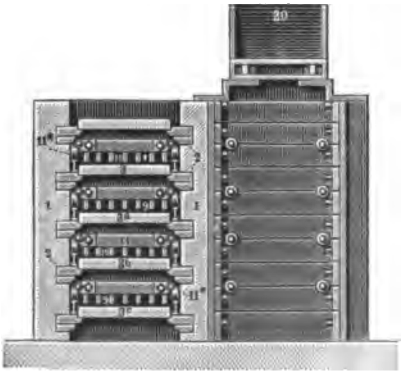


Fig. 109.

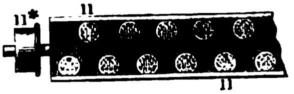
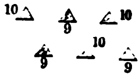


Fig. 110.

Fig. 111.



the stirring and conveying instruments must be reversed as regards their faces in succeeding beds. The teeth of the rakes are mounted in angle-iron bars, 11, provided with rollers, 11*, which run upon rails, 12, carried by the projecting supports 2. To each of these angle-bars are connected rods, 13, attached at their other ends to a frame or carriage, 14, provided with wheels, 15, which run upon rails, 16, on the floor, the said rods being supported and guided by grooved pulleys, 17. On the carriage, 14, are fixed toothed racks, 18, situated outside the furnace, and supported at their outward ends by rollers, 19, and in gear with these rods are pinions, 20, on a shaft, 21, driven by motive power. Motion being communicated to the shaft, 21, the pinions, 20, cause the racks, 18, to traverse the frame, 14, which, as stated, travels on the rails, 16, and thus the rods, 13, are caused to traverse the rakes or conveyers along the several beds of the furnace. According to the positions shown in the drawings, the carriage 14 is in its outward, or nearly outward, position, and the flat ends of the instruments will have delivered a certain amount of material through the opening 4 on to the bed 3*a*, the same operation having taken place with regard to the opening 6 and bed 3*c*. The carriage now running inward, the sharp points of the ploughs will simply stir the material on the beds 3, 3*b*, while the blunt ends on the floor 3*a* will deliver a certain quantity of material through the opening 5 on to the bed 3*b*, and at the same time the instruments on the floor 3*c* will pass an amount of completely calcined material into the receptacle 8, to be removed at pleasure. The feeding of the furnace takes place in the following manner:—At F is a channel leading to the top floor 3, and above this channel is a hopper, 20, into which the ground material is from time to time fed. The bottom of this hopper is provided with a sliding plate, 26, having a ledge at its inner end, as seen in fig. 107. This plate is connected with rods, 22, swung upon arms, 23, and each having two stops, 24, 25. According to the position shown, the material rests upon the ledge of the plate, 26, which, when the carriage runs in, is pushed forward by its arrival in contact with the stops 24, and this action delivers a certain amount of material through the channel F. On the return motion of the carriage the stops 25 shift the plate 26 back, and so on. Instead of plate 26, there may be a winged bottom to the hopper. The furnace may be single or double, the latter (which is shown in the drawings) being preferred. The shaft 21 is connected by means of suitable gearing to any source of motive power, so that it may be rotated first in one direction and then in another, and thereby traverse the rakes alternately from one end of the furnace to the other. The rakes may move continuously; but it is preferable that they should remain stationary periodically in the position shown in the drawings, as they are then clear of the ore and out of the direct action of the heat, thereby suffering less injury from corrosion.

A number of these furnaces have been put up by the Sulphur Mines Company of Virginia, at Baltimore. According to a communication kindly made to me in May 1888 by the President, Mr. Crenshaw, three double furnaces were connected with a set of chambers of 180,000 cubic feet capacity, with Glover and Gay-Lussac towers, and two other furnaces with a set of 126,000 cubic feet. The 5 furnaces were to burn 14 tons of 47/48 per cent. pyrites each 24 hours, down to less than 2 per cent. of sulphur in the cinders.

It is mentioned as a drawback of Spence's furnaces that at the back end a collection of dust takes place by which the rakes are prevented from doing their work properly. Bartsch, of Bridgeport (Fischer's Jahresb. 1886, p. 256), consequently applies to the furnace ends a separate set of broad plates, moved by a second moving-frame in such a way that the dust is cleared out automatically every time the principal frame is made to work.

As stated in Zsch. f. angew. Ch. 1894, p. 134, I have met with several Spence furnaces at work in America, but they did not give general satisfaction. A variety of this furnace has been patented in America by A. C. Johnson, of Baltimore, where the moving parts are protected from heat (U.S. P. 642,334).

The ordinary shelf-burner has been combined with a mechanical arrangement by Hering (G. P. 9634), who feeds the top shelf continuously by means of a screen, the burnt ore being removed from the bottom shelf by another screw.

T. Mason (E. P. 3196, 1880) employs a furnace with a bed slanting slightly downwards, across which a number of fluted rollers (say 20) are lying, made of cast-iron or stoneware, moved by means of gearing outside the furnace. The pyrites-dust is fed mechanically into a hopper, situated at the upper end, and is gradually moved down the inclined hearth by means of the fluted rollers, the cinders being discharged at the lower end. A furnace placed below gives additional heat in the case of poor ores. (It is not likely that such an arrangement would stand the wear and tear unavoidable in this case.) Modifications of this furnace are contained in the patent No. 1788, of 1881, and No. 2831, 1882.

Walker and Carter (E. P. 4000, 1883) employ for roasting pyrites a set of eight horizontal cylindrical retorts (four tiers of two each), heated outside by an ordinary coal fire, and communicating by openings at alternate ends. Hollow shafts, provided with stirrers, pass through each retort; cooling-water runs through all these shafts from one to another and prevents their warping. Special contrivances prevent the stirrers from touching the sides of the retorts in spite of unequal heating. The broken ore is fed into the top retorts and gradually finds its way into the three following tiers; a current of air traverses the retorts in the opposite direction. This apparatus is stated to have worked well for roasting pyrites containing 42·2 per cent. sulphur (Engineering and Mining Journal, xxxvii. p. 294), but it does not convey the impression that it would go on for a long time without very heavy wear and tear; and the necessity of an outside fire also militates against it. The report made on this burner by W. Martyn (J. Soc. Chem. Ind. 1885, p. 26) is not encouraging.

W. Brückner (Engineering and Mining Journal, xxxvii. p. 425; Fischer's Jahresb. 1884, p. 221) employs for roasting pyrites-smalls the principal of a horizontal cylindrical revolving furnace. As this furnace is provided with internal firing, and the SO_2 gets mixed with all the smoke-gases, it is hardly intended, and certainly not adapted, for serving in the manufacture of sulphuric acid. This is, on the contrary, the aim of an apparatus patented by R. & C. Oxland (E. P. No. 7285, 1885), who roast the pyrites in a revolving cylinder of 30 feet length heated from the outside, so that the SO_2 is kept apart from the smoke-gases. At the lower end of the rotating tube is a cast-iron prolongation, heated externally by a fire-grate and flues. The amount of air admitted to the calciner is regulated by a contrivance in the end plate of the prolongation, which is also fitted with a door for the removal of the cinders. (This apparatus seems to be more intended for roasting arsenical ores, and recovering the white arsenic in the process.)

K. Walter has constructed a special burner for "*peas,*" that is, small pieces of ore between the size of a hazel-nut and such as pass through a sieve with eight holes to the lineal inch. This apparatus is described and figured in the 1st edition, pp. 225 to 229. It has grate-bars laid sideways across the burner, cast with projections beneath, through which a bar passes. This makes it possible to turn all the bars at the same time and exactly in the same way. The spaces between the bars can therefore be made very small, so that the "peas" do not fall through without the bars being moved; and as they lie only 6 inches thick, the air can pass through with the ordinary draught. Each compartment, with a grate surface of 32 square feet, burns from 14 to 20 cwt. in 24 hours.

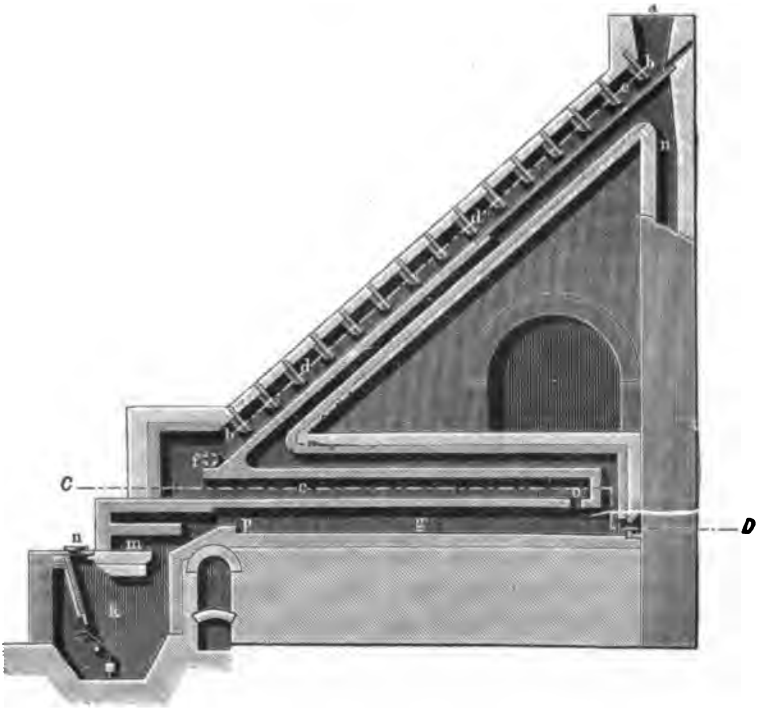
Walter's burners require a strong draught, and must be worked for a separate set of chambers; with insufficient draught very large scars are at once formed. As they are only adapted for a special size of ore, they have not met with any extended application.

4. FURNACES FOR ROASTING ZINC-BLENDE.

Zinc-blende is now the most important of all zinc-ores, and all of it must be converted into zinc oxide by a thorough roasting. This is nothing like so easy as with pyrites, as, on the one hand, blende contains at best only about 33 per cent., sometimes down to 18 per cent., of sulphur, and, on the other hand, it is much more difficult to burn out than iron or copper pyrites, zinc sulphate being formed, which is very difficult to decompose. As the manufacture of zinc requires nearly all the sulphur to be driven off, and as the burners employed for pyrites are useless in the case of blende, the latter was formerly roasted in reverberatory furnaces, all the sulphur dioxide passing away with the furnace-gases. This would probably be done even now, if the damage produced by the acid smoke had not caused the sanitary authorities, both in England and on the Continent, to impose upon the manufacturers the duty of doing their best to condense the acids contained in the smoke, the damage caused by which has been described *suprà*, pp. 154 *et seq.*

The development of the processes for abolishing the acid-smoke nuisance and utilizing the sulphur in connection with the roasting of blende, at least in one of the most industrial parts of Germany, has been described at length by Robert Hasenclever (Zeitschr. des Vereins deutsch. Ingenieure, 1886, p. 83; Fischer's Jahresb. 1886, p. 257), of whose paper we give a short abstract. Before 1855 all the blende consumed at the large Stolberg zinc-works was roasted in ordinary open furnaces by a direct coal-fire, the gases from which contained only about 0·75 per cent. SO_2 by volume and escaped into the atmosphere. In 1855 the Rhenania chemical works at Stolberg erected a furnace, intended to utilize the larger portion of the SO_2. This furnace, the invention of Friedrich Hasenclever, was the first by which the gases from roasting blende could be utilized for the manufacture of sulphuric acid. It consisted of a long muffle-furnace in which the ore was shifted along the hearth from back to front by manual labour (evidently identical in principle with Spence's first furnace, *suprà*, p. 330). Thus half the sulphur could be utilized for the manufacture of sulphuric acid, but with great waste of nitre. Godin improved this furnace by placing a series of muffles on the top, which the ore had to pass gradatim: but this apparatus was given up again for the Gerstenhöfer furnace (*suprà*, p. 332). By this, comparatively rich gases were obtained, but the immense quantity of flue-dust was very troublesome, and it proved too difficult to combine this furnace with another for finishing the roasting. After this several arrangements were tried by Hasenclever and Helbig, but these showed various drawbacks; and this led in 1874 to the construction of a new furnace, which has been fully described and illustrated in the first edition of this work, pp. 201 to 204; we describe it only briefly here (fig. 112). It consisted of a reverberatory furnace, *g*, on the top of which was placed a muffle, *c*, reaching all over its length. The bottom of this muffle, forming the top of the rever-

Fig. 112.



beratory furnace, was heated directly; the flame of the furnace, passing over the roof of the muffle, heated this as well, and then passed under an inclined plane at an angle of 43°, at the top of which, at *a*, the fresh (powdered) blende was fed in. The ore, on sliding down this plane (partitions, *d, d*, preventing its transit from becoming too rapid), underwent a preliminary heating by the hot gases passing underneath ; this heating was continued in the muffle *c c*, where air was admitted and as much of the sulphur was burned away as possible. At last the semi-burnt ore was pushed down into the furnace *g*, where it was burned completely by the fire from the gas-producer *k*. The sulphur dioxide formed here is certainly lost, and it constituted no inconsiderable portion (generally more than one third) of the whole; but that formed in the muffle and on the inclined plane is strong enough to be carried into lead chambers and converted into sulphuric acid, certainly at no great profit, if any.

A large number of Hasenclever furnaces were erected on the Rhine and in Silesia, but they were found to utilize on an average only 60 per cent. of the sulphur as sulphuric acid. The remaining 40 per cent. SO_2, being mixed with the fire-gases, still escaped into the atmosphere and were blamed for even more damage than they actually caused, the part played by the numerous zinc-works, glass-works, &c. being generally overlooked by the public (comp. pp. 82 & 83). We shall return to this subject in the 7th section of this chapter.

All these furnaces have become obsolete by the construction of blende-roasting furnaces, *which permit of utilizing the whole of the sulphur of the ore in vitriol-chambers,* and thus do away with the extremely troublesome processes for absorbing SO_2 from fire-gases. All these modern furnaces have one principle in common: they combine the heat produced by the burning of the blende sulphur with heat applied externally, but in such manner that the fire-gases are kept entirely separate from the roasting-gases. It has been found that this indirect heat suffices for completely roasting the blende.

The furnaces which first realized the principle of utilizing all the sulphur of the blende in vitriol-making, by completing the roasting by means of indirect fire, were invented by M. Liebig, who had the idea of constructing a sort of shelf-burner with shelves partially hollow and heated by indirect fire. His invention (G. P.

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21032 of Eichhorn and Liebig) is described and illustrated (from the patent specification) in our second edition, pp. 273–275 Comp. also Eichhorn's report in Fischer's Jahresb. 1889, p. 332.

We omit the description of the original style of these furnaces in favour of a modification known as "Rhenania furnaces," because they were constructed at the Rhenania Chemical Works at Stolberg (managed by R. Hasenclever). These are now widely used, not merely for blende, but also for other poor sulphur-ores in the state of smalls or even of "peas" (pieces up to ¼-inch diameter), and for metallurgical products (matte) of the same kind (p. 363).

The Rhenania furnace is shown in figs. 113 to 116, in a shape in which it has been used for several years, and which embodies the same principle as the furnaces actually at work at present, which merely differ from the above in details, to be mentioned below. These furnaces require two men per shift, and roast about 4 tons blende per 24 hours, with a consumption of 16 cwt. of coal. The temperature of the top muffle is 580° to 690°, that of the following muffles 750° to 900°. The progress of roasting is shown by the following percentages of sulphur:—

Raw ore	19·2	26·8		26·5	
End of first muffle	17·6	19·1	to 21·9	15·9	to 21·4
,, second ,, ...	12·0	11·2	,, 14·3	9·9	,, 12·4
,, third ,, ...	3·4	1·02	,, 1·48	0·75	,, 1·06
,, roasting	0·6	0·35	,, 1·02		—

In the case of richer ores the second muffle does not require heating; the fire-gases may be conducted below the third muffle without a partition, and then at once over the second roasting-bed.

Jahne (Zsch. f. angew. Ch. 1894, p. 305) describes some experiments made with these furnaces. They are greatly improved by arranging a partition cutting vertically through all three muffles and thus dividing the furnace into two parts, without any change in the firing. This admits of roasting 30 per cent. more ore down to the same percentage of sulphur and saves labour. It is best to build two furnaces back to back. On the top beds the ore is spread in layers twice as thick as on the bottom beds, leaving small gaps between the charges, to prevent their getting mixed. It takes three or four days before a batch charged at the top is discharged at the bottom. The raking over and moving on of the batches, following upon the discharging of a finished batch, requires 4 hours. The most careful work must be bestowed upon the finishing of the batches in the hottest place; this lasts at best 1½ hours, usually 3 to 4 hours, sometimes 7 to 8 hours. Tests are made by adding hydrochloric acid to a sample, and looking for any evolution of H_2S. The sulphur can be brought down to 0·1 or 0·2 per cent.; it ought never to exceed 1 per cent., except in the case of blendes containing limestone, which may retain 2 or 3 per cent. S in the shape of calcium sulphate. In regular work a charge of 9 to 12 cwt. roasted ore is drawn every 6 hours. 100 parts of raw blende average 85 of roasted ore, and require 25 or 26 parts of good coal. The furnaces are provided with large dust-chambers, which must be cleaned every few weeks. The dust consists mainly of zinc sulphate and calcium sulphate. Lead oxide is carried farthest, even through the ten cylinders of a Hargreaves plant connected with the furnace at Stolberg, right into the earthenware receivers of the acid-condensing plant. If the blende contains mercury, that metal is found in the mud of the vitriol-chambers connected with blende-furnaces, and can be recovered from it by distillation.

In Chem. Ind. 1899, p. 25, Hasenclever gives some more details respecting the Rhenania blende-furnaces, which now roast 4700 kils. blende in 24 hours with two men per shift. Only for poor ores the fire plays round all the muffles; generally the ore is roasted in three superposed muffles and the fire plays only round the top and bottom muffle. Two furnaces are built back to back. In order to avoid annoyance to the men, there is a space of 25 feet between two opposite furnaces. Six furnaces are connected with one set of chambers, their flues being built closely together, to keep the heat, until they unite just in front of the Glover tower.

Pierron (Mon. Scient. 1900, p. 562) states that at the Vieille Montagne the consumption of fuel is only 18 kils. per 100 blende of 25–28 per cent. S (with hand-furnaces or mechanical furnaces?).

Jensch (Zsch. f. angew. Chem. 1894, p. 50) shows by analyses that the sulphur in roasted blende is mostly contained therein in the shape of ferrous sulphide; when roasting down to 2 per cent. S, no ZnS is present, and it is therefore quite unnecessary to drive the roasting down to 0·5 per cent. S, as is sometimes demanded.

At Oker (1902) all "fines" of the ores used there (p. 85), passed through a 7 millim. sieve, are roasted in Rhenania blende-furnaces. Each furnace roasts from 3·55 up to 5 tons ordinary ores or matte, according to whether the roasting is driven to 3 or to 7 per cent. S in the residue; and from 3 to 4·5 tons regulus, according to whether 2 or 6 per cent. S is left in the residue.

At Freiberg the Rhenania furnace is used (1902) for pyrites smalls and "peas" down to 5 millim. size (¼ inch), for blende, recently also for matte and speiss, containing about 20 per cent. S, 25 per cent. Cu, and 20 per cent. lead. For ores containing rather more sulphur the furnaces are provided with three muffles directly superposed. The fire-flue passes underneath the hearth of the bottom muffle, rises up at the end of this and along the ends of the second and the top muffle, and returns along the roofing-arch of the latter, so that the fire-gases heat only the bottom of the lowest and the top of the highest muffle. For poorer ores the furnaces have only two muffles, the fire-gases passing both under their top and over their bottom and between both muffles. With such furnaces, whether containing two or three muffles, the sulphur in the cinders from pyrites "fines" is brought down to 2 per cent., from pyrites "peas" to 3 per cent., from blende to 1 per cent., from matte and speiss to 5 per cent. Each furnace takes 3½ to 4 tons ore per 24 hours, with a consumption of about 12 cwt. lignite and 6 cwt. coal; the work is done by two men per shift of 12 hours.

At Stolberg, in 1902, each furnace turned out 8 tons of roasted blende per day, with four men per shift, two on each side, and from 14 to 18 per cent. coal of the weight of roasted ore. The blende must be crushed to pass through a sieve of 2 millim. meshes. The product in the absence of lime shows 0·5 to 1 per cent. S, in the presence of lime correspondingly more. The roasting is stopped when a sample, treated with hydrochloric acid, does not stain lead paper. Sulphates (apart from calcium sulphate) are most easily formed when the furnaces do not go hot enough, *e. g.* after stopping for Sundays; once formed they are never completely decomposed.

Bémelmans (Germ. pat. 76775) describes a furnace for roasting both pyrites and blende in separate compartments; the sulphur vapour obtained from pyrites, sometimes by addition of coal, is utilized for removing from the blende (which must not be mixed with coal) arsenic, antimony, and phosphorus in the shape of volatile sulphides.

Michel Perret (G. P. 37842) has modified his well-known furnace for burning fuel in the shape of dust so as to roast blende, without mixing the fire-gases with the gases evolved by the burning blende. The principle is very similar to that of Eichhorn and Liebig.

Mechanical blende-burners are the following:—The burner patented by J. Haas (G. P. 23080) is very similar to MacDougall's (comp. p. 343), but the single chambers, in lieu of having simple brick bottoms, are separated by flues through which pass the fire-gases from a coal-fire. Mechanical stirrers move the ore from the top shelf over three others and ultimately into an open hearth, where the last roasting takes place.

Hegeler's burner is a combination of an Eichhorn and Liebig's burner with a stirring arrangement somewhat similar to Spence's (p. 352), but differing from it in some important practical details. This furnace works most successfully at Mathiesen and Hegeler's zinc-works, La Salle, Ill. It treats 35 or 40 tons blende with 28 per cent. S in 24 hours.

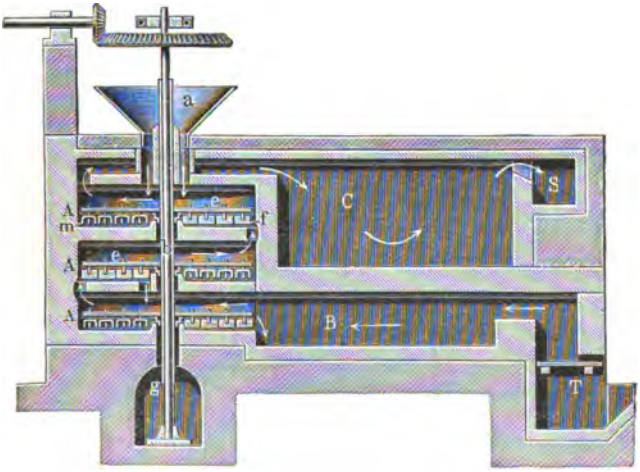
A mechanical blende-roasting furnace patented by the Chemische Fabrik Rhenania (G. P. 61,043) has not been actually erected (Chem. Ind. 1899, p. 26). Hitherto in Europe no other but the Vieille Montagne mechanical blende furnaces seem to be at work.

The burners patented by the Société Vieille Montagne (G. P. 24,155 and 36,609) are mechanical burners in which the flame of the coal-fire is not separated from the roasting-gases. These burners have been continuously at work at Oberhausen since 1883. Their construction is shown in fig. 117. There are several superposed circular calcining-hearths, A, A, to which is attached a square calciner B. The ground ore is charged through hopper *a* by means of feeding-rollers and flues on to the top chamber and gradually finds its way downwards and into B. The fire of the fuel burning on grate T first passes over B, then over the circular hearths A, A, into the dust-chamber C and into the flue S. The agitation is procured by the vertical shaft *b* and arms *e*, *e*, the stuffing-boxes being packed with asbestos. Shaft *b* is contained in an outer pipe *g*, and the air rising between them acts as a cooling medium. The arms carry tooth-rakes *m* in a radial position for the purpose of stirring, and slanting solid rakes *f* which move the ore from the circumference to the centre, or the other way, as is required for the purpose of gradually transporting the ore downwards and ultimately on to hearth B. [These furnaces, which had to be frequently repaired and made much flue-dust, are being gradually replaced by hand-worked muffle-furnaces.]

The furnaces or kilns for roasting ordinary copper-ores, lead-ores, and so forth, as far as they are not mentioned pp. 311, 312, and 357, cannot be described in this book, as they belong to the domain of metallurgy proper, and in these cases the roasting-gases are, if at all, sent into vitriol-chambers merely to get rid of them, but without the expectation of profitable work.

We merely mention a few modern attempts to obtain workable roasting-gases from such ores by new methods.

Fig. 117.



Huntington and Heberlein (E. P. 8064, 1896; 3795, 1897) obtain SO_2 by a new treatment of lead-ores, but in such a way that their conversion into sulphuric acid seems to be almost impossible.

Sébillot (E. P. 21,616, 1898) charges cuprous or other sulphur-ores, mixed with fuel, into a furnace provided with air-blast. The gases are taken into a chamber containing coke, pumice, or a suitable metallic oxide, where they are treated with air and steam, and where sulphuric acid is formed (comp. Chap. XI.).

Treatment of complex ores containing blende.—Hart (Journ. Soc.

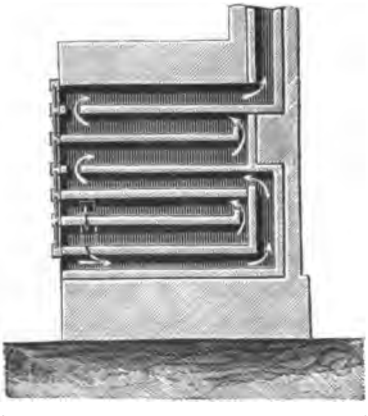
Chem. Ind. 1895, p. 544) proposes treating such ores with sulphuric acid in a saltcake pot, and when the mass has become pasty transferring it to a blind roaster and finishing it there, all the gases going into vitriol-chambers. The zinc remains behind as sulphate, which can be obtained by lixiviation and crystallization; or else it is mixed with poor zinc-ore and roasted, in which case the oxygen of the sulphate combines with the sulphur of the blende. The reaction seems to be:

$$ZnS + 4SO_3 = ZnSO_4 + 4SO_2.$$

5. BURNERS FOR THE SPENT OXIDE OF GAS-WORKS.

The spent oxide is now generally washed, so as to obtain ammonia salts therefrom, and is also frequently treated for the ferrocyanide or sulphocyanide. At all events the sulphur, which it contains in the free state, sometimes up to 50 per cent., is ultimately burnt for the manufacture of sulphuric acid. This is sometimes done in ordinary brimstone-burners, as shown *suprà*, p. 268 *et seq.*; but in this case it is difficult to burn it out completely, and there is loss of sulphur in the cinders. Ordinarily it is burnt in apparatus very similar to "shelf-burners," as shown in fig. 118 (Hill's burner). Each chamber in this case is about 10 feet long, 20 inches wide, and 9 inches high. MacDougall's and Herreshoff's mechanical burners (pp. 343 & 349) have also been employed for this purpose.

Fig. 118.



Cowen's burner, figs. 119 and 120, consists of a row of fire-clay gas-retorts,* and requires no further explanation. Other works are said to burn that material in burners with very narrowly-placed grate-bars.

Fig. 119.

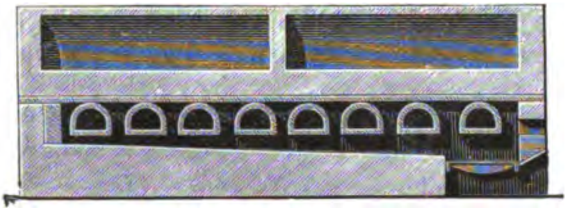
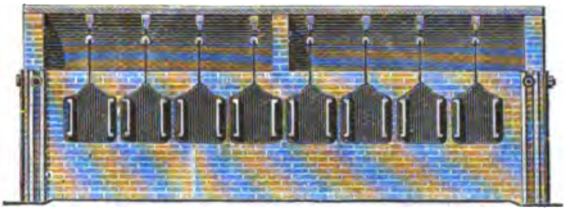


Fig. 120.



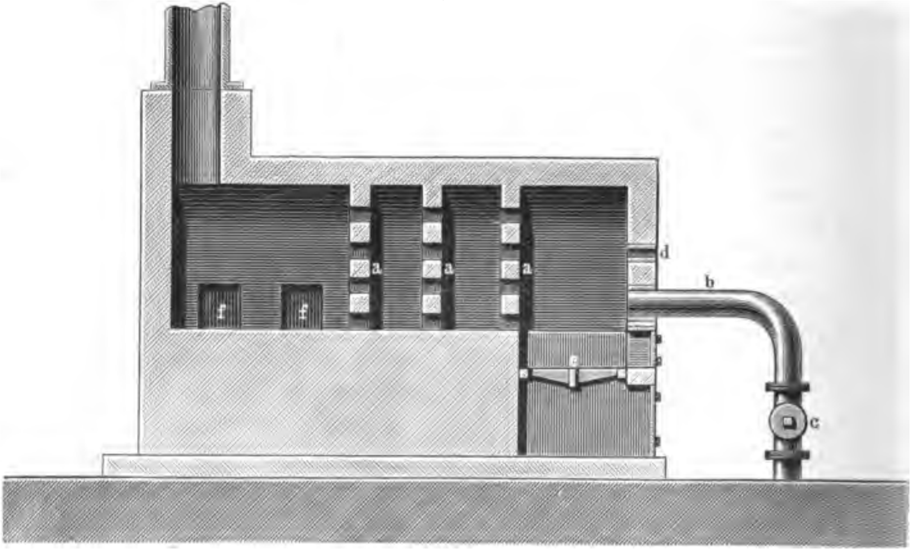
Sometimes the oxide is moulded into bricks and put into lump-burners; it burns off very well and the cinders fall through the grate-bars by themselves; in fact, the bars must be touched as little as possible. This process does not answer so well as shelf-burners.

The 38th Alkali Report, p. 97, recommends not to discharge the hot residue from oxide burners through the front working-doors, as this causes a nuisance, but to push it into chambers placed at the back, where they can cool off. The gases should be led through long, heated flues, in order to burn the tarry substances and ammonia which destroy nitre.

6. Burners for Sulphuretted Hydrogen.

These are usually of a very simple description. As shown in fig. 121, they consist of a brick chamber provided with some baffling-walls *a, a*. The sulphuretted hydrogen gas (which is nearly always mixed with a large quantity of inert gas, chiefly nitrogen) is introduced by the cast-iron pipe *b*, the supply being regulated by an inlet-valve *c*. Air is admitted partly round the pipe *b*, partly by a special opening *d*, which ought to be provided with a slide or other means of regulating the amount of air. The heat produced by the combustion of the sulphuretted hydrogen is quite sufficient for keeping the temperature of the chamber at a red heat, so that the gas is always lighted again if by chance the flame has been extinguished. This is aided by the baffling-walls *a*, *a*, which serve both the purpose of supplying a reservoir of heat for the just-mentioned purpose, and of mixing the gases so as to insure perfect combustion. The grate *e* is required only for irregularly composed gases, like those formed in the saturation of the gas from ammonia-stills by sulphuric acid; especially for re-lighting the gas after stoppages over Sundays, and so forth. With gases of regular composition and comparatively rich in sulphuretted hydrogen, like those given off in Chance's sulphur-recovering process, the grate *e* is quite unnecessary, as these gases are as easily lighted and kept burning as coal-gas. The doors *f f* serve for "potting" the nitre, where it is not preferred to employ more rationally constructed apparatus for this purpose (comp. Chapter V.). The size of the whole chamber may be about 10 to 12 feet long, 4 or 5 feet wide, and 3 feet high. Pans for concentrating sulphuric acid may be placed upon it, and even in this case the gases will issue hot enough to do full work in a Glover tower. Sublimation of sulphur is never observed with ordinary

Fig. 121.



care in admitting the air. One very great advantage in burning sulphuretted hydrogen is this: that, contrary to the variations in the amount of SO_2 in burning brimstone or pyrites, even when keeping up a regular rotation of the burners, there is in this case a perfectly continuous process, as the supply of H_2S from the gas-holder is continuous; the amount of air need never be varied when once regulated; the percentage of SO_2 in the burner-gas is altogether uniform; the chamber process is consequently much more regular than with brimstone or pyrites, and the consumption of nitre is correspondingly smaller. All this, however, holds good only if the percentage of H_2S in the gas is practically constant, whilst with gases of very varying composition, such as those evolved in ammonia-works, the very contrary is the case.

It must be remarked that at some works, in burning the sulphuretted hydrogen from the Chance process, an increased consumption of nitre has been noticed, whilst at others a saving in nitre in comparison with the burning of pyrites has been effected. Evidently in the former case the quality of the sulphuretted hydrogen has not been as it ought to be; it has no doubt varied in percentage, and may even have contained a notable quantity of carbon dioxide, so that the chamber-process would not be as regular as desirable. Sometimes it has been noticed that the combustion has not been quite perfect, so that sublimed sulphur has been found in the Glover tower or even in the chambers; but this is evidently owing to mistakes and careless work, and should not occur with ordinary care.

In 1886 E. Lombard (Monit. Scient. 1889, p. 1231) described a shelf-burner for sulphuretted hydrogen, consisting of two separate compartments, 7 ft. 6 in. deep inside. There are four shelves, 6 ft. 6 in. long and 1 ft. 4 in. wide, formed of four fire-clay slabs each. The top shelf is perforated with many holes, and occupies the whole length and width of the furnace; the other shelves are not perforated, and leave at alternate ends a passage of 12 × 16 in. for the gases. Each furnace is provided at the base with four burners for H_2S and two air-tubes, disposed in two tiers of three each, the air-tubes occupying the central places. The burners consist of fire-clay tubes, 6 ft. 6 in. long, 1½ in. wide inside, and ⅜ in. thick, projecting two-thirds of their length into the furnace, and provided on the top with slits or holes for dividing the gas. They are connected in front by a cast-iron tube with a stop-cock for regulating the flow. The air-tube is 2½ in. wide, and is provided with an iron thimble for regulating the quantity entering. The gaseous products of combustion pass into a flue, 1 ft. 6 in. × 2 ft., on the top of the furnace, then into a small dust-chamber, and then into the Glover tower. Total height 6 feet. The pressure of the gas is = 1½ inches of water; it is said to work very well.

Simpson and Parnell (E. P. 14,711, 1886) regulate the supply of air and gas in any desired proportion, so as to obtain either free S or SO_2, by employing two vessels, each of which is provided with an inlet and an outlet valve. Both vessels are filled and emptied simultaneously by a mechanical arrangement, the two vessels acting in conjunction, so that the gas entering and leaving one of the vessels bears a constant proportion to the quantity of air entering and leaving the other vessel. [Such an arrangement, very useful as it undoubtedly is for the production of free sulphur from H_2S, seems unnecessarily complicated when the object is that of burning the H_2S with an excess of air for the purpose of sulphuric-acid manufacture.]

7. PROCESSES FOR ABSORBING SULPHUR DIOXIDE CONTAINED IN ACID-SMOKE, FIRE-GASES, AND THE LIKE.

The abatement of the nuisance caused by the acid-smoke given off in metallurgical and other operations presents special difficulties where the percentage of acids is so slight that their utilization by condensation or by conversion into sulphuric acid is out of the question; that is, if less than 4 per cent. SO_2 by volume is present. The damage done by such acid gases has been described in Chap. III. p. 154 *et seq.*

A survey of the processes tried a number of years ago at Stolberg for dealing with acid-smoke has been given by Hasenclever (Fischer's Jahresb. 1881, p. 173). All of these will be mentioned below; they all have one common feature: they are very expensive, and at the same time they hardly ever attain their purpose completely.

The problem of dealing with the enormous quantity of sulphur dioxide contained in *ordinary coal-smoke* has been hardly ever attacked in a serious manner, as the expense and inconvenience of any imaginable measures for this purpose have hitherto appeared to be quite unbearable; and it does not seem as if this would be different in the near future. The only practicable remedy in this case, as well as in some cases of metallurgical smoke, is to dilute the gases with a large quantity of air, by erecting very tall chimneys for carrying them up to a considerable height above the surface of the earth. Such chimneys have been made up to 450 feet in height. In the case of hydrochloric acid they have entirely failed in their object (comp. Vol. II.), but in that of sulphur dioxide the dilution of air is more efficient. Freytag certainly estimates (somewhat arbitrarily) that smoke is harmless only when it does not contain beyond 0·003 per cent. SO_2 by volume; but as, for instance, in lead-works the percentage of SO_2 in the main flues, where all the smoke and fire-gasses are mixed, rarely exceeds 0·1 per cent., it is very likely that, if these gases are allowed to escape only 200 feet or more above any vegetation, they get sufficiently diluted with air in their descent to become harmless. This is owing to the fact that sulphur dioxide diffuses pretty equally in the air, whilst hydrochloric acid, sulphuric anhydride, acid salts, &c., which form visible fumes, generally reach the bottom in a very little divided stream, and cannot therefore be made innocuous by very tall chimney-shafts. In fact, this is the only explanation why the scores of tons of sulphur dioxide daily belched forth in certain localities by lead-works, zinc-works, glass-works, &c., have not ere now destroyed all vegetable life around the works, which is notoriously the case only in a few isolated instances. But as such instances do occur, and as altogether the requirements of sanitary authorities are constantly becoming stricter, the removal of the acid-smoke to a high level by means of chimneys cannot be pronounced a final solution of the difficulty, even where only SO_2 is the acid concerned, all the more as in moist weather the acids escaping from the very tallest chimneys are brought down to the ground in a somewhat concentrated state.

A proposal has been made by Wislicenus and Isaachsen (G. P. 124,900) to dilute smoke-gases to such an extent that the amount of acid contained in them becomes innocuous. This is to be attained by building within the chimney-stack a second lower stack, provided with pipes carried up and downwards. Air is introduced into the inner stack and escapes partly at its top, partly through the up and down pipes, thus intimately mixing it with the chimney gases. [It is not likely that this process can be carried out in many cases as prescribed above, but it is stated in the 38th Alkali Report, p. 76, that bringing down the percentage of acids in the exit gases from chemical works by means of diluting them in the chimney with air is not contrary to the law.]

O. Schott (Dingl. Journn. ccxxi. p. 142) has proposed *to utilize the sulphur dioxide given off in making glass from sodium sulphate for the manufacture of sulphuric acid.* The gas is to be made richer in sulphur by employing for the glass-mixture gypsum in lieu of limestone. Sulphate of soda, gypsum, and coal are to be mixed in proper proportions, and brought to a bright red heat in muffle-furnaces or in elliptical glass pots, until the SO_2 is driven off. The fritted residue of sodium and calcium silicate is to be powdered and used by glass-works; the gas is to be conducted into lead chambers and worked for sulphuric acid. This process seems entirely impracticable; especially since such diluted gas (mixed with a great deal of carbon dioxide) has not yet been utilized.

Thirion (Fr. P. Feb. 28, 1874; Wagner's Jahresb. 1875, p. 391) makes a similar proposal for heating sodium sulphate with coal and silica, whereby a mixture of sulphur vapour, sulphur dioxide, and carbon monoxide is cooled. The sodium silicate is to be decomposed by CO_2 or to be used as such. [As a proposal for manufacturing sulphur or sulphuric acid this process is evidently hopeless.]

We will now give a synopsis of the various methods for treating ordinary acid-smoke, with special reference to the removal of SO_2 and SO_3. For details we must refer to the sources quoted in this work, to a special treatise by C. A. Hering, 'Die Verdichtung des Hüttenrauches' (Stuttgart, 1888), and to one by Schnabel, 'Metallhüttenkunde,' ii. pp. 58 *et seq.*

Condensing by water seems to be the simplest and most obvious process, looking at the great solubility of sulphurous and sulphuric acid in water. But this process is in reality only practicable where the percentage of acids is not too slight; dilute acid-smoke is not sufficiently washed without employing a comparatively enormous quantity of water; and, surprising as it is, SO_3 is even more difficult to condense in this way than SO_2. It is quite certain that condensation by water can be made to *pay* only where the gases are sufficiently concentrated to convert them into sulphuric acid in lead chambers; it is therefore the interest of smelting-works, &c., to conduct their processes in such a manner that the acids are diluted with as little inert gases as possible. If the percentage of SO_2 reaches 4 per cent. by volume, they may be submitted to the Schroeder and Haenisch process (*vide infrà*), or they may even be converted into sulphuric acid, although this will hardly leave any profit at that percentage; but it is enough to have removed the nuisance. Where, however, there is less than 4 per cent. of SO_2 in the gases, any *utilization* is out of the question; the thin acid liquids obtained by washing the smoke must be run to waste (which in most cases means a fresh nuisance, and is not permitted by the authorities); nor is the SO_2 and SO_3 anything like completely taken out of the gases; and the nuisance is at best only diminished, but not remedied.

At all events the contact of the absorbing-water with the acid gases must be made as intimate as possible. The condensing-apparatus used for hydrochloric acid, and described in Vol. II., act only for somewhat strong gases; the weak gases which we are here treating of require special means, such as paddle-wheels or similar spray-producing apparatus, costly to work and to keep in repair, and generally imperfect in their action. Haworth (U.S. P. 268,793, of 1882) proposes to condense the SO_2 given off in lead-smelting by water, boiling it out of the solution and taking it into a lead chamber—an economically hopeless process.

In lieu of water, Freytag (G. P. 9969, 14,928, 15,546) and Hasenclever (G. P. 17,371) employ somewhat concentrated *sulphuric acid*, in an ordinary coke-tower of large size. This agent retains the SO_3 much better than water, so that in some cases the expense of working the process is paid by the sulphuric acid gained. SO_2 is also retained to some extent, but only if the gases have been well cooled. The necessity of doing this and of previously removing the flue-dust, which is sometimes very difficult to perform, is a great drawback to this, as well as to all corresponding processes. In fact Freytag's process has been abandoned again; at the best it could remove only a small portion of the injurious constituents from the acid-smoke. (Schroeder and Haenisch, Chem. Ind. 1884, p. 118.)

Absorbing the acids by caustic lime, generally in the shape of a cream of lime, is one of the oldest and, if properly carried out, still one of the most efficient ways of removing the acid-smoke nuisance. Where the quantity of acids is but slight, and the manufacture in question is sufficiently profitable otherwise, this process is even now applicable, and if properly applied it does remove practically all the acids. The cream of lime should meet the gases in a finely divided state, either by flowing down properly-constructed towers, or, still better, by being converted into a spray by means of paddle-wheels or the like (comp. Rayner and Crookes' patent, E. P. 2678, 1875). That this leads to the desired effect, even with the large quantity of SO_2 emitted in roasting blende, has been proved by working on the large scale in Upper Silesia (comp. Bernoulli, Fischer's Jahresb. 1880, p. 184). But unfortunately the expense of this process, where large volumes of acid gases are concerned, is very serious, more especially as nothing like the whole of the lime can be utilized for absorption, and the attempt to utilize the product as bisulphite of lime (Hasenclever, G. P. 10,710) has failed (comp. Schroeder and Haenisch, Chem. Ind. 1884, p. 118).

According to Jensch (Fischer's Jahresb. 1889, p. 321) the deposit forming in the milk-of-lime towers contains so much lime that it can be used over again, and at least a product is obtained containing 37·7 per cent. lime, 38·4 SO_2, 2·8 SO_3, 4·1 CO_2, &c., which is very useful as an addition to animal manure for the purpose of fixing the ammonia, in which respect it is equal to gypsum.

It has been found by Cl. Winkler and other observers that the SO_2 in smoke is much more injurious to vegetation if accompanied by much steam, *e. g.* in smoke-gases from brick-kilns. Spitta (G. P. 110,388) proposes to absorb SO_2 and steam at the same time by passing the gases up and down several flues, into which slaked lime in the shape of dust is injected from the top. The bisulphite of lime formed is removed from the bottom of the flues by means of special doors.

Egestorff's Salzwerke (G. P. 70,396) describe a very efficient apparatus, consisting of a series of chambers with inclined bottoms, connected with collecting-tanks. The alkaline absorbing liquid is pumped up over and over again and brought into contact with the gases by means of a spray-producer.

Limestone is very much cheaper than caustic lime, and is almost equally efficient if employed in the proper way; that is, if a very large surface of limestone is exposed to the acid gases, and if this surface is kept from being covered with a crust of sulphite by being constantly washed with a stream of water. Cl. Winkler has constructed a special arrangement for this purpose (G. P. 7174), which completely fulfilled its object at the Schneeberg ultramarine works. It consists of three brick chambers filled with large pieces of limestone, the roof being formed by plank covers perforated with many holes, through which water is kept running on to the limestone. The gases pass through these chambers successively and in regular rotation. The absorption of SO_2 is excellent, but as each cwt. of sulphur requires 3 cwt. of limestone, it is still too dear for most metallurgical purposes, especially as any utilization of the sulphur is out of the question.

The limestone treatment is frequently employed at sulphate-of-ammonia works for getting rid of the SO_2 formed by combustion of the H_2S escaping from the saturators. This treatment is frequently mentioned in the Alkali Inspectors' Reports, and in the 36th Report (for 1899), pp. 25 & 26, Mr. R. Forbes Carpenter, the Chief Inspector, states the following conditions as being absolutely necessary for success:—1st. There must be sufficient draught at the furnace, and the suction at the condenser outlet must be adequate to supply this at all times, to avoid sublimation of sulphur. Such draught might be supplied by injecting air under slight pressure in the furnaces. 2nd. The gases must be completely cooled before and behind the furnace. If they enter the limestone-tower above 38° C., much calcium sulphate is produced, which forms a protective crust on the limestone. The hot gases are to be cooled first by cast-iron pipes until some condensation takes place, when leaden pipes must be substituted for them. 3rd. The limestone-tower should be made of wood planks, tongued and grooved, or of brick and cement, not of cast-iron. [The latter material would surely not be dreamt of by a chemical engineer in such a case, but possibly it has been used in gas-works!] 4th. The supply of water is best made in two forms, one constant, the other intermittent (by flushes), especially in the case of limestone, but with hard chalk the intermittent flush only may be used, at not too long intervals. [Comp. the much better feeding methods for Gay-Lussac and Glover towers described in Chap. VI.]

Precht (E. P. 3443, 1881) employs for absorbing SO_2 from gaseous mixtures either *magnesium hydrate* or *aluminium hydrate*, especially the former. It is either spread upon trays moistened with water, or is brought into contact with the gases (previously cooled to 100°) in the state of a cream, in an apparatus provided with a mechanical agitator, or in columns like those employed for treating sulphuric acid by sulphuretted hydrogen (Chap. X.). This produces a crystalline precipitate of magnesium sulphite, besides a solution of magnesium sulphate. On heating the magnesium sulphate to upwards of 200° the SO_2 is split off, and can be condensed as such or converted into sulphuric acid, whilst magnesia remains behind, together with about 3 per cent. magnesium sulphate. The latter is heated with coals, and thereby converted into MgO, remaining behind, and a mixture of SO_2 and CO_2, which is utilized in vitriol-chambers [?]. M. Lyte (J. Soc. Chem. Ind. 1882, p. 165) gives a detailed description of this process with diagrams. It has been tried at several places, but has evidently been found too little advantageous for most purposes.

Alumina is included in Precht's patent, but is less efficient than magnesia. Sometimes acid gases have been passed through layers of clay-slate (schist), whereby sulphate of alumina has been formed, but this process is evidently only practicable under special local circumstances.

Zinc carbonate or *oxide* was proposed by Schnabel (Fischer's Jahresb. 1882, p. 266), who had previously made manifold attempts at the Lautenthal smelting-works for treating the acid-smoke, all without any sufficient success. Ultimately a process was adopted (G. P. 16,860), consisting in passing the gases over basic zinc carbonate moistened with water. Zinc sulphate is formed, which, on heating (preferably mixed with coal), yields sulphur dioxide, to be converted into sulphuric acid in lead chambers, and a porous residue, consisting of a mixture of zinc oxide with basic zinc sulphate. Schnabel's apparatus is rather complicated, and the result not very satisfactory; the process is very troublesome to carry on, and costs much more than the value of the sulphuric acid obtained (a provisional protection, No. 5416, 1881, for this process was taken out in England by M. Lyte).

Fleitmann (G. P. 17,397) passes the sulphurous gases, together with some air, through a kiln containing a mixture of *ferric oxide* and coal. The latter, in burning, yields the necessary heat, and at the same time reduces the Fe_2O_3 and SO_2, so that FeS collects at the bottom (the success of this process is more than doubtful).

Metallic iron, moistened by water, was employed by Winkler (G. P. 14,425), but was not found practicable for dilute acid gases. Thorp (E. P. 8862, 1889) again recommends towers filled with scrap-iron, and kept moist with water or a solution of ferrous sulphate, the temperature being maintained at from 49° to 71° C.

Metallic copper or zinc, in very finely divided form, was tried at the Frankfort gold-parting works, but without sufficient success; but at the same works the following interesting process was worked out.

Rössler (Dingler's Journal, ccxlii. p. 278; Fischer's Jahresb. 1881, p. 184) showed that gaseous mixtures, containing, besides a large excess of air, far too little SO_2 and SO_3 for being treated in vitriol-chambers and otherwise not treatable in any efficient manner, can be completely deprived of both the above acids by forcing the gases, by means of a Körting's injector and a perforated coil of pipes, *underneath a column of water,* holding some *copper* in suspension or some *cupric salt* in solution. The cupric sulphate acts as a carrier of the oxygen of the air upon the SO_2, and large quantities of sulphuric acid are formed in this way, so that this process might even be employed for manufacturing sulphuric acid. At Frankfort, however, it is carried out in this way, that the tank into which the gases are passed is always supplied with precipitated copper, from which by this process cupric sulphate is obtained without any expense. Rössler has also applied this principle to the treatment of ordinary acid-smoke (G. P. 22,850), by combining a whole set of apparatus. This process is very adversely criticized by Friese (Chem. Ind. 1895, p. 137), who has made a long series of experiments with it, with totally negative result. No oxidation of SO_2 with air to SO_3 by the catalytic action of $CuSO_4$ could be proved. SO_2 reduces a hot solution of $CuSO_4$, with intermediary formation of cupric sulphite, to metallic copper. A smooth and easy oxidation of the cupric sulphite to sulphate does not take place. Hence this process would be useless for the production of cupric sulphate, and still more so for that of sulphuric acid.

A special class of processes utilizes the reaction between *sulphur dioxide* and *hydrogen sulphide,* either both being in the state of gases, or the latter being in the nascent state as evolved from sulphides. The reaction in its simplest form is:

$$2\,H_2S + SO_2 = 2\,H_2O + 3\,S\,;$$

but, apart from the fact that polythionic acids are formed by secondary reactions, the above reaction is anything but complete with very dilute gases. Details about it will be given in Vol. III. in the chapter treating of the recovery of sulphur from soda waste; in this place it may suffice to mention that a patent founded upon the above reaction was taken out by Landsberg (G. P. 6364) in connection with the roasting of blende.

When sulphides are employed, the reactions are even more complicated, but the absorption of SO_2 can be made more complete.

Cl. Winkler (Fischer's Jahresb. 1880, p. 245; more details in Chem. Ind. 1880, p. 126) describes a very interesting process for dealing with the gases from an ultramarine-works containing much SO_2. They were brought into contact with a solution of *sodium sulphide,* obtained from the sulphate going to waste in that manufacture, by reducing it with coal. The SO_2 is completely absorbed, with formation of sodium thiosulphate, or, in another modification, with formation of free sulphur; but on the large scale sodium tetrathionate was formed, which had to be decomposed by heating into sodium sulphate, SO_2, and free sulphur. *Theoretically* nothing was consumed but coal, but evidently a very large amount of fuel must have been used in the various evaporations and furnace operations, with an amount of skilled labour out of proportion to the value of the products obtained. After having been used from 1868 to 1877, the process just described was abandoned for a simple absorption by limestone moistened with water (p. 374). Even before Winkler, in 1864, Jacob had carried out for some years a similar process to that just described, employing either sodium or calcium sulphide, at Münsterbusch (Fischer's Jahresb. 1881, p. 181).

Calcium sulphide, proposed many years ago by Dumas, forms also the absorbing substance in Kosmann's process (G. P. 13,123). By reducing calcium sulphate with coal and lixiviating a solution of calcium sulphydrate is obtained [?], which in very finely divided state is brought into contact with the gases containing SO_2. The result is the formation of sulphur and gypsum:

$$5\,SO_2 + 2\,CaH_2S_2 + 2\,H_2O = 7\,S + 2\,CaSO_4,\ 2\,H_2O.$$

The sulphur is extracted from the mixture by superheated steam. and the gypsum returns into the cycle of operations [it is very doubtful whether this would succeed!]. From further communications by Kosmann (Fischer's Jahresb. 1882, p. 270), it appears that the absorbing medium was afterwards prepared by boiling sulphur with milk of lime, that is, as the ordinary "liver of sulphur," and that the whole process was entirely in the experimental stage (from which it does not seem to have emerged).

Barium sulphide, which was experimentally tried at Freiberg, proved much too costly.

Vegetable charcoal is proposed by A. H. Allen (B. P. 189, of

1879), who passes the gases, freed from dust, through drying-towers fed with sulphuric acid and then through columns filled with charcoal, previously ignited in a stream of nitrogen, where the SO_2 is retained, whilst the nitrogen passes on. By a vacuum or by heating to 300°–400°, or by a combination of both, the SO_2 is to be driven out and utilized. (This process, apart from the prohibitory expense, is hardly practicable, because the gases in question contain nearly always a large quantity of oxygen which will convert the SO_2 to a great extent into sulphuric acid within the pores of the charcoal.)

A totally different way of employing coal is used in one of the oldest processes for dealing with acid-smoke, namely, *passing the gases through red-hot coals*, in order to reduce the SO_2 to sulphur. This has already been mentioned in Vivian's pamphlet, "Proceedings of the Subscribers to the fund for obviating the inconvenience arising from the smoke produced by smelting copper ores" (London, 1833), and in a pamphlet of Reich's, describing the experiments made at Frankfort in 1858, and it has been proposed over and over again, with the same negative results. A new apparatus, by Schroeder and Haenisch (G. P. 33,100), is said to give good results, nearly the whole of the SO_2 being reduced to S; but their process evidently works only with rich gases, and does not deal with those poor gases which concern us here.

Bémelmans (Germ. pat. 77,335) converts the SO_2 by reduction with carbon and hydrogen into H_2S, dries this by the process to be described below, mixes it with dry SO_2, and converts them into H_2O and SO_2.

8. PREPARATION OF SULPHUR DIOXIDE IN THE PURE STATE *.

Formerly pure SO_2, free from nitrogen and excess of oxygen, was required only in very few cases for industrial purposes. The methods employed for preparing that gas were various, one of the commonest being the action of concentrated sulphuric acid upon copper at a higher temperature. This is, of course, only applicable where there is a sale for the cupric sulphate formed, and is, moreover, hardly workable on a large scale. Cheaper and easier is the process of heating strong sulphuric acid with charcoal, when

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* A special treatise on the preparation, properties, and application of pure sulphur dioxide is 'Flüssiges Schwefeldioxyd,' by A. Harpf (Stuttgart, 1900).

a mixture of SO_2 with CO_2 (and CO) is obtained:—

$$2\,SO_4H_2 + C = 2\,H_2O + 2\,SO_2 + CO_2.$$

The CO and CO_2 are harmless in many applications of SO_2. Sulphur dioxide, quite free from other gases, is made by heating concentrated sulphuric acid with sulphur:—

$$2\,SO_4H_2 + S = 2\,H_2O + 3\,SO_2;$$

this can be done by running a slow stream of sulphuric acid on sulphur, heated to about 400° in an iron retort. It should, however, be noticed that melted sulphur acts very strongly upon cast-iron; hence another process, privately communicated to me from a trustworthy source, would seem preferable. The operation is performed in a cast-iron pan, widening out at the top so that a lining of acid-resisting bricks can be put in it. Concentrated sulphuric acid is boiled with sulphur, which floats on the top and is kept by the brick lining from coming into immediate contact with the iron, whilst the lower part of the pan is fully exposed to the heating action of the fire.

Sulphur dioxide was made by the Compagnie industrielle des procédés Raoul Pictet (G. P. No. 22,365), and was purified in a special apparatus, utilizing the fact that the hydrates of SO_2 all crystallize at −10°, and that gaseous SO_2 at this temperature loses all its aqueous vapour. We refrain from describing this (somewhat complicated) apparatus, which is also described in the Journal of the Society of Chemical Industry, 1883, p. 413, as the condensation of liquid SO_2 is performed in a much simpler way by the Schroeder and Haenisch process, which in fact has caused the above-mentioned process to be abandoned.

P. Hart (E. P. 13,950, 1885) prepares pure sulphur dioxide by acting with strong sulphuric acid, of spec. grav. 1·750, on finely ground iron sulphide, both being mixed in a cast-iron retort and heated to over 200° C., when a steady stream of nearly pure SO_2 is evolved.

An old and well-known process for obtaining pure SO_2 is: heating ferrous sulphate with sulphur, with a little air, the reaction being:

$$2\,FeSO_4 + 2\,S + 3\,O = Fe_2O_3 + 4\,SO_2.$$

This process was made the subject of a new patent by Terrell (B. P. 5930, of 1884), who evidently lays the greatest stress on the ferric oxide remaining behind, which furnishes a good paint.

Ford's process (Am. Pat. 363,457; Chem. Zeit. 1887, p. 721) consists mainly in burning sulphur by means of air previously dried with sulphuric acid, and passing the gases through a worm, where, by cooling and pressure, liquid SO_2 is condensed. It is difficult to see any novelty whatever in this process.

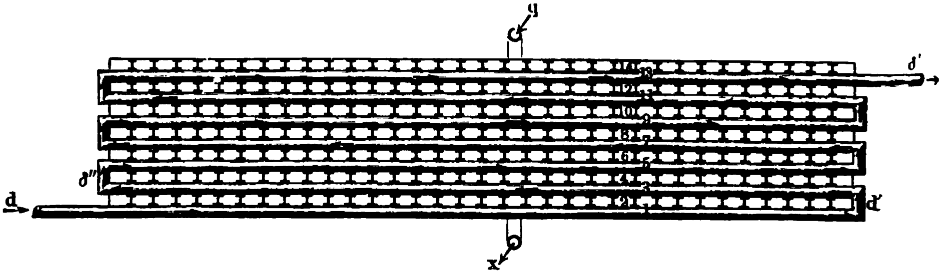
The only process for preparing pure liquid sulphur dioxide on the large scale is at present that of Schroeder and Haenisch, which allows of preparing that substance in a cheap way from gases containing down to 4 per cent. SO_2. It is unnecessary to say that richer gases are better for this purpose. This process has made liquid sulphur dioxide a cheap article, manufactured on a large scale, and has rendered it possible to employ that substance for many purposes for which formerly only the ordinary impure gaseous SO_2 was available.

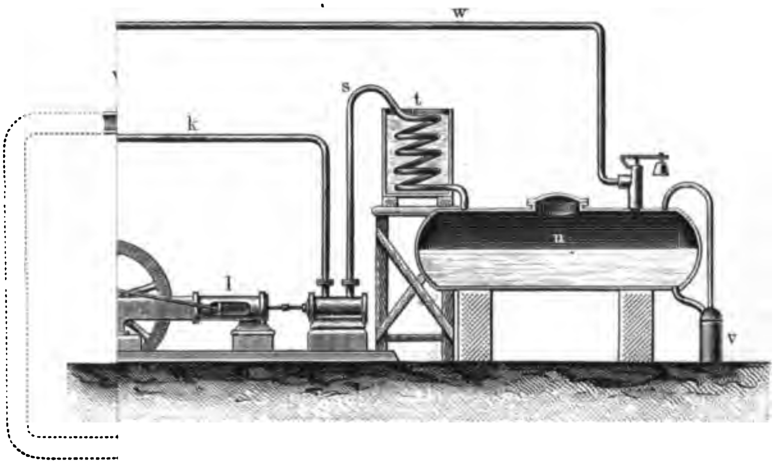
The process of Schroeder and Haenisch, embodied in B.P. 2621, 1883; 6404 & 6405, 1885, was first taken up by the firm Wilhelm Grillo (afterwards converted into the Aktiengesellschaft für Zink-Industrie, vormals Wilhelm Grillo) at their zinc-works at Hamborn, Rhenish Prussia, where, in 1885, an experimental factory was erected, turning out about 12 cwt. liquid sulphur-dioxide per diem. The gases, testing 6 per cent. SO_2, were taken from a novel kind of blende-roasting furnace, similar to that described on p. 361 (system Julius Grillo, G. P. 28,458). In 1886 four such furnaces were combined with a larger plant for 8 tons SO_2 per diem. Very soon after similar factories were erected at Lipine and at Chropaczow, in Upper Silesia, and about 1899 another at Bound Brook, N.J., U.S.A. (The factory at Chropaczow has since been converted into an ordinary sulphuric-acid works.)

The process consists in absorbing water in an ordinary coke-tower, and expelling it again from the resulting weak solution by the action of heat, in such manner that the latent heat of the steam carried along is fully utilized, and ultimately a very small amount of coal is required. It is described by the inventors, apart from the patent specifications, in 'Chemische Industrie,' 1884, p. 120; but this description is now antiquated, and we shall here go by later descriptions (Paper Trade Journal, 1888; Zsch. f. angew. Ch. 1888, p. 488), by personal observations of the work as practically carried out, and by notes received from the inventors in 1902.

The burner-gases arrive in the flue *a a* (fig. 122), and after having lost part or most of their heat by passing underneath the lead pans *e e*, they pass into the coke-tower *b*, where they are treated with such a quantity of cold water that all the SO_2 is condensed (the exit gases contain only 0·05 per cent. SO_2 per volume), and only O and N pass out at *c*. The solution of sulphurous acid, containing about 10 kils. SO_2 per 1000 kils. of liquid, is run out by pipe *d*, and first passes through an apparatus, shown separately in fig. 123, where it receives a previous heating, and then successively through the closed lead pans *e e*, where the heating is continued by the action of the hot burner-gases acting in the flue *a a*. The apparatus, fig. 123, serves for heating up the cold acid solution by the heat of the spent liquor, resulting at a later stage of the process. It is built up by superposing a number of sheets of lead, 7 lbs. per superficial foot, of considerablė surface, corresponding to the quantity of acid liquor to be treated. These sheets are combined in such a way as to form a corresponding number of shallow lead chambers, about 1½ inches deep, superposed one over another and connected with each other in the following way :—The acid liquor flows through *d* into the bottom chamber from left to right; through a side connection *d'*, occupying the whole length of the lateral edge, it is conveyed into the third chamber, from here through *δ''* into chamber 5, and thus further cools the 7th chamber, 9th, and so forth, issuing at *δ'*. The chambers Nos. 2, 4, 6, 8, and so forth, serve in the same way for running down the hot spent liquor obtained at a later stage of the process. This liquor, which enters at *q*, always flows in a direction at right angles to that of the acid liquor rising up in the alternate chambers, so that the connections for the spent liquor flowing down are situate in the front and back part of apparatus fig. 123. In

Fig. 123.

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order to prevent a sagging of the plates, strips of lead are arranged in each chamber as stays, running in each chamber in the direction of the current of liquor. The thin sheets of lead being good conductors of heat, the cold acid liquor, on rising through chambers 1, 3, 5, 7, &c., is gradually heated up, whilst the hot spent liquor, descending through the intermediate chambers, gives off its heat. Of course there must always be a certain difference and loss of heat, depending upon the duration of contact, the depth of the liquid, and the speed of the current. With chambers of 1½ or 2 inches depth, and counter currents lasting 10 or 12 minutes, and sufficiently large surfaces, the difference of temperature will be about 10°; that is, the cold acid liquor will be heated up from 15° to 85° C., whilst the hot spent liquor goes down from 95° to 25° C. In practice the heating up rises to 95°, and the cooling liquid descends to 50°. The cold spent liquor is run to waste through *x*.

Quite recently (1902) the flat lead chambers, where leaks are not easily discovered and repaired, are replaced by a set of small lead cylinders working on the system of gradual heat-exchange (counter-current).

The heated-up acid liquor now travels successively through the covered lead pans *e e*, where the heating is continued as mentioned before, so that the boiling-point is attained. The gases and vapours here evolved are conducted through pipe *f* into the water-cooled worm *g*, and from here through the pipe *h* into the tower *i*, where the last remaining admixture of moisture is taken out by dry calcium chloride or (preferably) by coke moistened with strong sulphuric acid. From here the dry sulphur dioxide passes through pipe *k* into the pump *l*. The liquor heated to boiling in the pans *e e*, which still contains some SO_2, passes through pipe *m* into the column *n*, where the steam is to a great extent condensed by injection of cold water, whilst nearly dry SO_2 passes up in *p*, and thus equally gets into the worm *g* and further on into the pump *l*. The column *n* is shown in some detail, as described in a further patent by Schroeder and Haenisch (G. P. 36,721), which refers to the separation of steam from its mixture with SO_2, and as this is a matter of general importance, we shall give their statements at some length. It is not easy to separate large quantities of aqueous vapour from a mixture with gaseous SO_2. Indirect cooling by outward application of cold water requires a very large leaden apparatus, and the effect is but partial, as the vapours pass without hindrance through the central parts of the worms or other kind of apparatus. Moreover the condensed water, unless the temperature of the cooling-apparatus is kept nearly at a boiling heat, carried down very much SO_2. The new process effects the removal of the steam from the aforesaid gaseous mixture by direct injection of water, which certainly at first condenses a good deal of SO_2. But if the acid solution thus formed is made in a systematic manner to meet the hot mixture of aqueous vapour and SO_2, its temperature will be gradually raised and will ultimately attain boiling heat, and *pari passu* its percentage of SO_2 will decrease, so that at 100° it is nearly at zero. The following table shows the diminution of the percentage of SO_2 with the rise of temperature :—

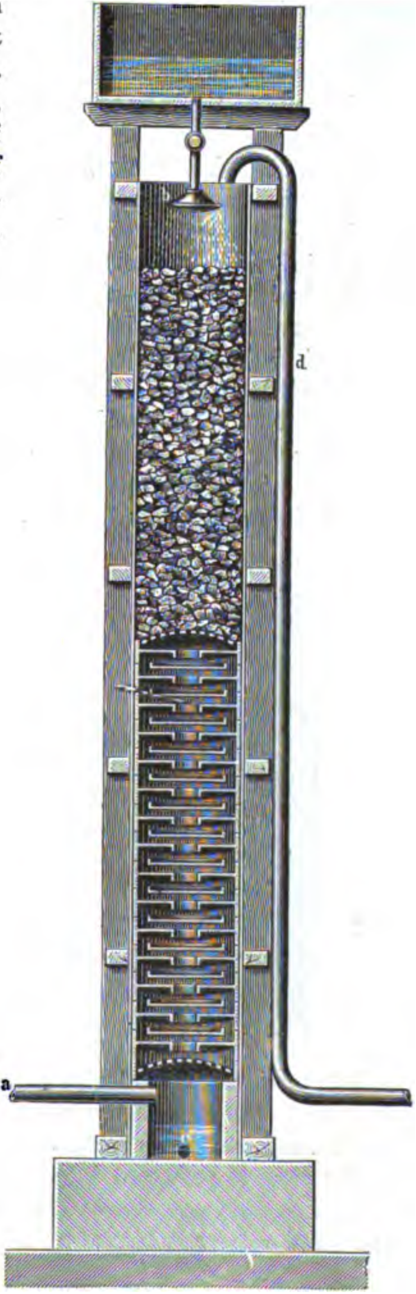
Percentage of a saturated solution of SO_2 :—

At 20° C. = 8·6 per cent. SO_2.
„ 30° C. = 7·4 „ „ „
„ 40° C. = 6·1 „ „ „
„ 50° C. = 4·9 „ „ „
„ 60° C. = 3·7 „ „ „
„ 70° C. = 2·6 „ „ „
„ 80° C. = 1·7 „ „ „
„ 90° C. = 0·9 „ „ „
„ 100° C. = 0·1 „ „ „

If the injection of water is so adjusted that the liquid running off is at a temperature of 95° or 100° C., the latter cannot, as shown by the preceding table, carry away any considerable quantity of SO_2. On the other hand, if the course traversed is long enough, the steam must be completely condensed by the cold water injected.

This process is carried out in the apparatus shown in fig. 124, viz., a leaden column, filled in the lower part with stoneware diaphragms, in the upper part with coke. The mixture of steam and SO_2 enters through pipe *a* and rises in the tower. Cold water is injected by the rose *b*, condensing both water and SO_2, and flowing down as an aqueous solution of sulphurous acid. On reaching the lower parts, it meets continually fresh quantities of hot gases and vapours, and arrives at the bottom 100° C. hot. It there yields up again the SO_2 absorbed higher up, and at the bottom pipe *c* carries off both the injected water and that condensed from the steam. After some time of working, and with proper regulation of the feed, the temperature of the water from the top downwards rises regularly to a boiling heat, and its percentage of SO_2 diminishes at the same ratio; but the quantity of SO_2 in the upper region is so considerable that the injected water cannot retain it all, and pipe *d* carries away a continuous stream of gaseous SO_2 deprived of steam. The dish shape of the stoneware parts in the lower half of the tower has the advantage of retaining the descending liquor for some time, and exposing it to the heat of the rising steam; but instead of this, coke may be used all over, if the tower is made high enough.

Fig 124.

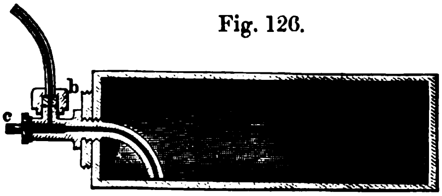


Returning to fig. 122, we see that the water condensed in the worm *g* finds its way equally into column *n*, and is deprived of its SO_2 there. The hot spent liquor runs off at the bottom by pipe *q*, and is utilized, as explained before, for heating up the cold acid liquor in the apparatus, fig. 123, where the entrance to the pipe *q* is visible. In order to regulate the compression of the gaseous sulphur dioxide to a liquid, a taffeta bag (*r*) is interposed in pipe *k*, and the motion of pump *l* is regulated according to the size of this bag. The compressed gas enters through *s* into the worm *t*, and is liquefied there by cooling and pressure, the latter depending upon the temperature of the cooling-water, *e.g.*, 1·26 atm. at 10°, 2·24 atm. at 20°, 3·51 atm. at 30°, &c. From *t* the liquid runs into the wrought-iron reservoir *u*, from which it is drawn off into the iron bottles *v* or into tank-waggons. In order to get rid of the carried-along portions of oxygen and nitrogen, the boiler *u* is provided with an outlet-pipe *w*, connected with *u* by a valve; the gases from here are conducted back into the absorbing-tower *b*.

Haenisch has also described an improved column for boiling the solution of SO_2 (G. P. 52,025). In 1899 a factory in Silesia produced 1266 tons liquid SO_2 by the above process from zinc-blende gases; the production of the other works is not known. The cost price is supposed to be £2 per ton (on somewhat arbitrary data); the selling price is £5 to £5 10*s*. at the works.

Fig. 125.

Fig. 126.



The liquid sulphur dioxide is sent out in iron cylinders (bottles) holding 1 or 2 cwt. each, or in tank-waggons of 10 tons capacity. The former are shown in figs. 125 and 126. When sent out, the outlet valve is protected by a cap *a*. Before use this is removed, as well as the small cap fixed on the neck *b*. If now the plug of the screw-valve *c* is turned by means of a key, the sulphur dioxide escapes in gaseous form through the opening in *b*. The stuffing-box or the whole valve must *not* be removed. After a time the evaporation of SO_2 lowers the temperature to $-10°$ C., so that no more gas is given off till the apparatus has taken up heat from without.

If the sulphur dioxide is to be got out in the liquid form, the vessel is put on its side (fig. 126) in such a position that neck *b* is at the top side. The pressure of its vapour now forces the SO_2 out of *b*. The bent tube within the vessel admits of emptying it entirely of liquid SO_2. This substance can be conveyed away by a lead pipe, screwed on to *b*, or even by an india-rubber pipe. The bottles are tested to 50 atmospheres pressure, so that there is no danger whatever in their transit, as the vapour-tension of SO_2 amounts to :—

0	atmosphere	overpressure	at	$-10°$ C.
0·53	”	”	”	0°
1·26	”	”	”	$+10°$
2·24	atmospheres	”	”	20°
3·51	”	”	”	30°
5·15	”	”	”	40°

Still, it is advisable not to keep the liquid in a place whose temperature may rise upwards of 40° C.

To prevent over-filling, in view of the expansion by heat, the bottles should not be filled more than nine-tenths, which is ascertained both by weighing them and by prolonging the outlet-tube inside to one-tenth of the depth of the vessel; when opening the valve only gas, no liquid, should escape. These bottles are usually made to hold 100 kils., exceptionally 500 kils. Besides, tank-waggons are used for 10 tons liquid sulphur dioxide, contained in three wrought-iron welded cylinders, about 23 feet long and 2 feet 3 inches diameter, tested for 30 atmospheres.

Boake and Roberts (Engl. pat. 19,789, 1892) find that liquid SO_2 does not act on tin or soft solder, and that therefore these can be employed in the manufacture of carrying-vessels.

Soy (Engl. pat. 12,276, 1893) patents the process of sending out liquid SO_2 in glass vessels sealed by the blowpipe, to be broken by a hammer in the rooms to be disinfected.

The principal uses for liquid sulphur dioxide are for refrigerating-machines (Pictet's and others), for wood-pulp manufacture (to bring the calcium bisulphite liquors up to strength), for the purification of beet-root juice, for disinfecting, for bleaching, for the manufacture of glue and gelatine.

Recently liquid sulphur dioxide has been applied by Behrend and Zimmermann as a means for increasing the efficiency of steam-engines by utilizing the heat of the exhaust steam for evaporating SO_2. The high-pressure vapours thus produced are utilized in an auxiliary cylinder for generating motive power, and are afterwards again condensed to liquid SO_2. Hitherto this system does not seem to have fulfilled its expectations.

The formerly rather extensive use for bringing calcium bisulphite liquor (for the manufacture of wood-pulp) up to strength has very much decreased, since the factories have improved their plant for the direct preparation of strong sulphite liquor.

The employment of the strong SO_2 obtained by the Schroeder and Haenisch process for manufacturing sulphuric anhydride (fuming O.V.) will be mentioned in the 11th Chapter.

The analysis of liquid sulphur dioxide is described in my 'Chemisch-technische Untersuchungsmethoden,' vol. i. p. 269.

9. DRAUGHT-PIPES AND FLUES.

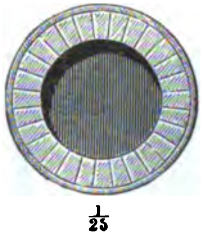
The flues leading the burner-gases from the kilns into the chambers or into the Glover towers may be constructed of brick-work only so far as the gases keep hot enough not to allow any moisture whatever to condense, that is especially in upright flues and flue-dust chambers. From this point they must be made of cast-iron, and further on, when they have got cooler, of lead.

The gas, which goes away red-hot from the burners, must necessarily be *cooled down* to the temperature of the chambers, say 60° or 80° C.; otherwise the first chamber would be very quickly destroyed. This cooling was formerly effected by conveying the burner-gas in very long flues of cast-iron, or partly of cast-iron, and, when partially cooled, of lead. Such cooling-flues were made up to 300 feet long.

The cast-iron pipes are suitably shaped, as shown in fig. 127, in order that the upper half may be replaced independently of the lower, or taken away for cleaning; the latter can also be done by means of man-holes. For a set of from 12 to 18 burners a pipe of 2 feet diameter is sufficient; but they are now and then made upwards of 3 feet in diameter. Sometimes they are lined with fire-bricks, as shown in fig. 128; the cooling in this case is very imperfect and the cost higher. Occasionally, in very large works, square or oblong flues of wrought- or cast-iron are found. Brick flues (for perpendicular shafts or for flue-dust chambers) are made of bricks boiled in tar, and set with tar and sand. Earthenware pipes mostly crack too quickly.

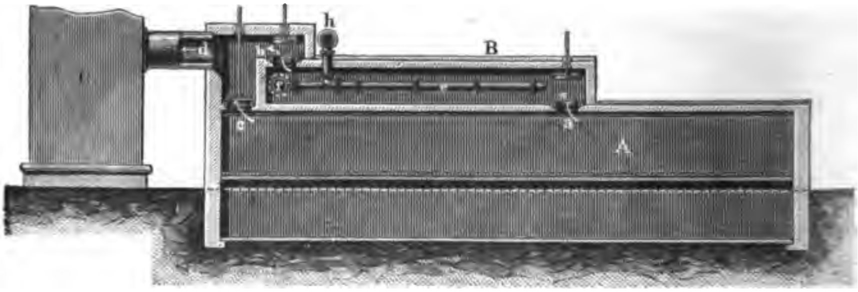
Fig. 127.

Fig. 128.



Perpendicular stacks and pipes act as a sort of chimney, and they are therefore carried up nearly to the top of the chambers where there is no Glover tower. These pipes were sometimes outwardly cooled by water, and even very complicated contrivances were met with for this purpose. It has long been recognized that the only rational way of cooling the burner-gas is this: taking away its heat for some useful purpose, and this is almost everywhere done in the Glover tower (Chap. VI.). Apart from this, the heat of the burner-gas is occasionally utilized for concentrating acid in lead pans (Chaps. IV. & IX.). Sometimes other ways of disposing of this heat are employed. Thus at the manure-works of Messrs. H. & E. Albert, at Biebrich-on-the-Rhine (see fig. 129), each pyrites-kiln A is surmounted by a gas-chamber B; the burner-gases enter by the holes *a*, provided with shut-off valves, and through similar openings (*b*) get into the pipe *d*, leading to the Glover tower C; a third opening (*c*) permits sending the gas direct into *d* and C. In each of the chambers B there are horizontal cast-iron pipes (*e*), branching off from a main pipe *f*, into which air is forced by a fan-blast. This air, being exposed to the hot burner-gases, becomes hot itself and leaves the chambers in order to be carried away by the main pipe *h*. This heated air is then conveyed to drying-stoves, where the superphosphate is dried by its action. At Albert's works the temperature of the air is brought to 100° C., but it may be kept cooler or hotter (up to 135°) by regulating the speed of the fan-blast. The burner-gas, entering through *d* into the Glover tower C, is still hot enough to do all the concentrating and denitrating work required; the Glover towers are not so overheated and require less repairs than formerly; the acid flows from them only at 115°–120°, against 140° as before the new arrangement, and requires less cooling for the Gay-Lussac towers. The saving in coals for the drying-stoves is 5 tons per diem (comp. the description, with further diagrams, in Zeitschr. f. angew. Chemie, 1889, p. 287; also E. P. of Albert, Fellner and Ziegler, No. 15,980, of 1888).

Fig. 120.



Flue-dust.

In the gas-flues and draught-pipes *flue-dust* is always deposited, much more when smalls are burnt than with lump ore, especially in furnaces where the small ore is moved about. In such cases special dust-chambers are indispensable, as has been remarked in the description of those furnaces. Even with large lumps the flues and pipes must be cleaned out from time to time, as they would otherwise be stopped up entirely. At some factories this is done monthly, at others more rarely. If the deposit is allowed to remain too long, it hardens into a stone-like mass, which cannot be got out without stopping the process.

The composition of this deposit varies, of course, very much; and even its external aspect varies from that of a dry, light dust, to that of a thick, strongly acid mud. Clapham analyzed such a deposit, from a source not mentioned (Richardson and Watts, Chem. Technol. i. 3, p. 70), and found:—

Sand, &c.	2·333
Lead oxide	1·683
Ferric oxide	3·700
Cupric oxide	trace
Zinc oxide	trace
Arsenious acid	58·777
Sulphuric acid	25·266
Nitric acid	trace.
Water	8·000
	99·759

D. Playfair (Chem. News, xxxix. p. 245) has examined flue-dust from pyrites-kilns, in which he found chiefly arsenic, antimony, lead, copper, and iron; of thallium 0·002 to 0·05, of tellurium and selenium 0·001 per cent. was present. He describes in detail the analytical methods employed.

Reich ('Erdmann's Journal,' xc. p. 176) found in the Mulden Works a crystallized deposit consisting of equal molecules of arsenious and sulphuric anhydride. Similar deposits have been frequently observed since.

In other cases the deposit is dry dust, mostly consisting of mechanically conveyed pyrites-dust, better burnt than that within the burner itself (Bode, 'Beiträge,' p. 41), and nearly always containing so much arsenic than its crystals can be seen with the naked eye.

H. A. Smith ('Chemistry of Sulphuric-Acid-making') found in the dust 46·36 per cent. of As_2O_3, along with a large quantity of sulphur in the pasty condition—the latter, of course, formed by sublimation from pyrites.

The flue-dust is also a principal source of *thallium*, as we shall see; and when *selenium* occurs in the pyrites it is found in the flue-dust.

The flue-dust from the roasting of blende is, of course, quite differently composed from that formed in burning pyrites. Such flue-dust contains (Fischer's Jahresb. 1882, p. 273):—

	I.		II.	
Zinc oxide insoluble	8·40	26·20	8·20	20·20
Ditto in soluble combination	17·80		12·00	
Ferrous oxide, soluble	2·16		2·52	
Ferric oxide, ditto	2·40		4·20	
Lead oxide	3·38		4·26	
Sulphuric acid, insoluble	6·46	24·89	8·04	26·88
Ditto soluble	20·43		18·84	
Water	6·59		9·00	
Residue (chiefly ferric oxide)	31·80		32·42	
	99·42		99·48	

Flue-dust from the St. Mardy Tinto Santarossa pyrites (comp. Lunge and Bänziger, *supra* p. 55) contained sulphur: sulphur free 0·13 per cent.; ditto as sulphide 1·48; SO_3 as free sulphuric acid and sulphates 16·31; As_2O_3 69·07; Sb_2O_3 1·68; CuO 0·14; Fe_2O_3 2·03; sand 2·65; water, traces of other substances and loss 6·51.

Bellingrodt (Chem. Zeit. 1886, p. 1039) has found in the flue-dust from roasting blende at Oberhausen (Rhenish Prussia) a sufficient quantity of *mercury* to make its recovery profitable.

Krause (G. P. 55,676) washes the flue-dust from blende-furnaces and tries to recover the zinc from the washings by precipitation with alkaline carbonates.

Where the quantity of flue-dust is very large, as is generally the case with arsenical ores, and with some of the burners for pyrites-smalls, the ordinary dust-chambers, which form simply enlargements of the gas-flue, are not sufficient, and special contrivances must be adopted here. This matter has been thoroughly worked out in the lead-smelting works and other metallurgical establishments, and a large number of apparatus has been constructed for this purpose. A very complete synopsis of this is given in the pamphlet by C. A. Hering: 'Die Verdichtung des Hüttenrauchs' (Stuttgart, 1888), pp. 8 to 36. Many of the contrivances employed at lead-works, &c., are unsuitable for pyrites on account of being made of iron. But the general principles remain the same: the flue-dust must be made to deposit by cooling, by retarding the speed of the gaseous current and by offering to it large surfaces to which it can attach itself. All these conditions are more or less fulfilled by making the gas-flues adequately long and wide, but this is not sufficient for "bad cases," especially for arsenical ores. The case is here complicated by the fact that the cooling of the gas may be injurious to the chamber process, and that the long flues, especially those carried in a zigzag way or provided with "baffle-walls," interfere very seriously with the draught. The latter disadvantage has been greatly lessened since it has been recognized that it is unnecessary to carry the gases in flues like those sketched in figs. 130 and 131 (in the former the diagram may be taken either as plan or elevation), where the current of gas is constantly checked by meeting solid surfaces, but that the surfaces may be disposed in the direction of the current itself, where they cause the dust to be deposited on them without interfering with the draught. Fig. 132 shows how this can be done in such a way that the flue-dust can be removed without interfering with the process. The gases arriving through *a* are, by means of dampers, sent either through chamber A or B. In the present case, the dampers *b b* being closed, the gases travel through A. Each chamber is divided into several longitudinal

Fig. 130.

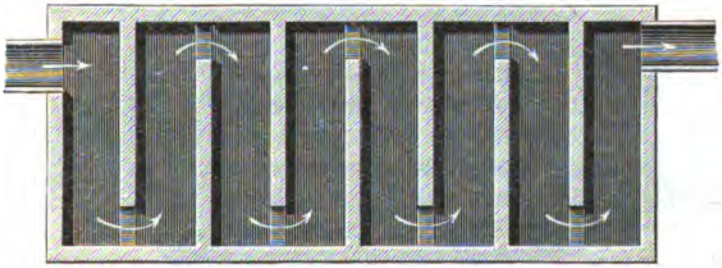
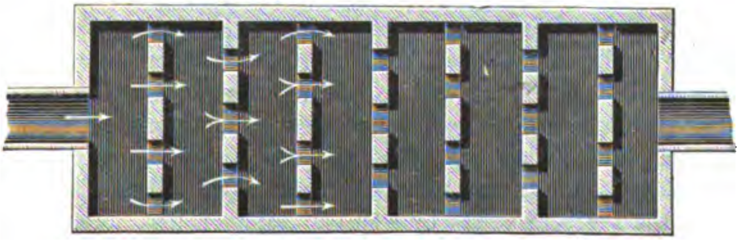
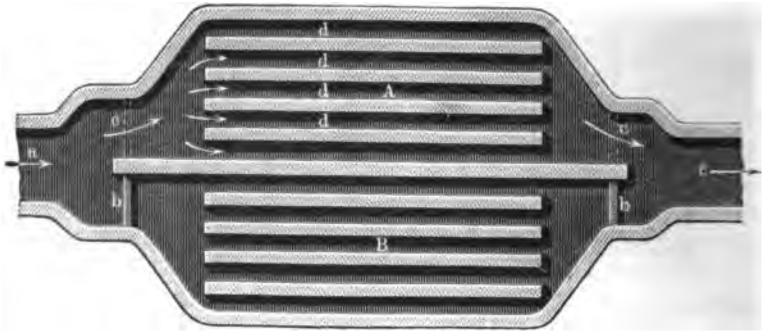


Fig. 131.



channels by thin partitions *d d*, made of masonry, fireclay slabs, lead, or other suitable material. The gas thus travels in parallel streams, without any check than that of the indispensable friction, and the streams collect again into one, issuing at *e*. When chamber A is too much choked up by dust, the dampers *b b* are opened, the dampers *c c* are shut, and the gases now travel through B, giving an opportunity to clean out chamber A by means of suitable man-holes.

Fig. 132.



In very bad cases, as, for instance, with mechanical dust-burners, longitudinal partitions are not sufficient, and real baffle-plates must be employed, as shown in figs. 130 and 131, and very much multiplied in figs. 100 and 101 (p. 347). In such cases the loss of draught must be sometimes compensated by mechanical means.

In many cases, where very large quantities of flue-dust have to be dealt with, the gases must be *cooled* artificially. This was done at the Freiberg works by a special kind of lead flue, cooled by water, as sketched in figs. 133 and 134, where the first represents a longitudinal section on the line A B, the second a sectional plan on the line C D. The sides of the flue are formed by a number of oblong pipes, *a a*, joined together at their narrow ends. On the top there is a shallow trough, *b*, supplied with a constant stream of water, which trickles down through holes, shown in the diagram, into the space *a a*, and from these through other holes into the common channel *c*, running lengthways. The bottom of the flue is not water-cooled, but as it rests on the small pillars *d d* it is exposed to the action of the air. These flues are very expensive to build, but they have been found to do their work very well indeed, and they need next to no repairs (detailed in the 'Freiberger Jahrbuch,' 1879, p. 151, table xii.). Of the

2 or 2½ per cent. of arsenic contained in the Freiberg ores, by far the greatest portion (97 per cent.) is condensed in these long flues, where the gases are ultimately cooled down to the temperature of the outer air.

Fig. 133.

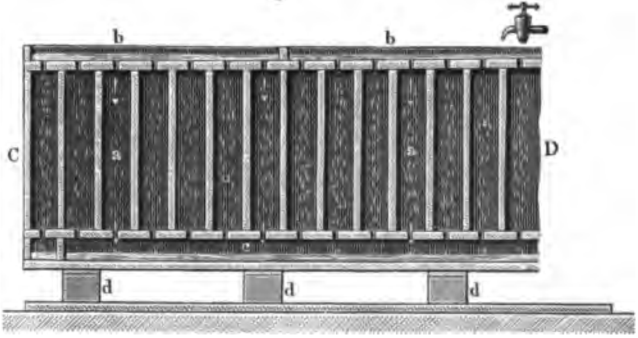
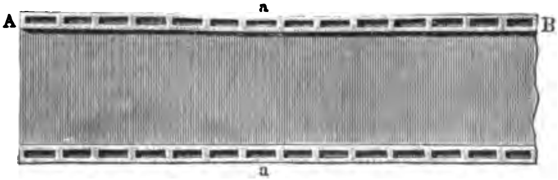


Fig. 134.



Bauer (Jahrb. f. Berg- u. Hüttenw. 1894, p. 39) states that the nine sets of chambers connected with the Freiberg smelting-works (containing 30 lead chambers) possess 8037 metres of flues, of 3·8 square metres section. The flue-dust in 1893 contained 1137 kils. silver, 1656 tons lead, and 917 tons arsenic, valued at £13,600. Eighty per cent. of the dust was recovered, 20 per cent. has hitherto been lost. The damages to be paid had diminished from £8050 to £180. In that year new flues on the Monier-Freudenberg system were built for recovering the last 20 per cent. of dust. The rate of cooling of the gases was 1° C. per 8·3 metres length in closed-in Monier flues, per 4·5 metres in freely exposed Monier flues, per 3 metres in leaden flues, and per 6 metres in brick flues.

In 1902 I am informed that the water-covered flues have been abandoned at Freiberg as being too costly, and have been replaced by simple lead tunnels. Where the heat is too great for the stability of the latter, brick flues are employed.

Falding (Min. Ind. ix. p. 623) describes a dust-catcher, constructed by A. P. O'Brien, of Richmond, Va., on the well-known centrifugal principle. It works in connection with the cast-iron fan of the same inventor, described in Chap. VI., and receives the gas from five Herreshoff fines furnaces, retaining 75 per cent. of the dust. At the same time it does very efficient service as a metre-oven. As shown in figs. 135 & 136, it consists of a tapering, hopper-shaped iron shell, 8 feet wide in the cylindrical part and 12 feet high, with a 6-in. opening in the bottom for the discharge of flue-dust. It is lined with 4 inches fire-brick. The gas enters through the top pipe at a high rate of speed from the fan and strikes the cylinder tangentially; it leaves the apparatus through a central pipe. The gas takes a rotary motion and deposits all the heavy dust, which is automatically discharged through the 6-in. opening. Six tubular metre-pots are arranged in the manner shown, so that they can be charged from the top and discharged sideways.

Fig. 135.

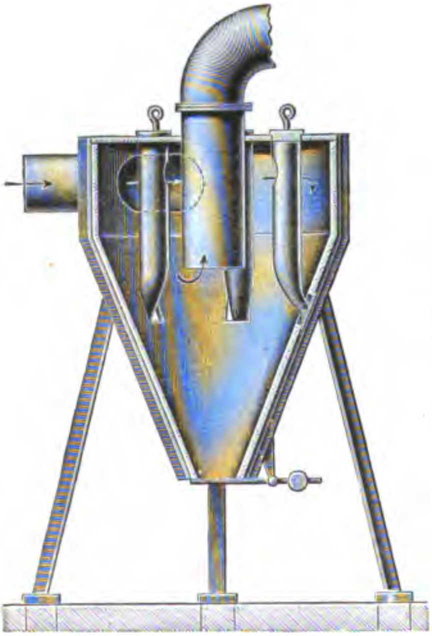


Fig. 136.

Sulphur Dioxide for the Manufacture of Wood-pulp ought to be as free as possible not merely from flue-dust but also from sulphuric acid (or sulphur trioxide, comp. next Chapter). For this purpose very efficient dust-chambers must be provided; the gas must also be specially cooled, *e. g.* by perpendicular cast-iron pipes, 2 feet 6 inches diameter, running up for a height of 50 or 60 feet and down again; they end in a lead-lined pipe provided with a manhole and filled with iron borings. Here the sulphuric acid, which is condensed by the cooling, collects, and is taken up by the iron borings. Provision must be made for removing the solution of ferrous sulphate formed, and for renewing the iron borings as they waste away. (A description of such an apparatus is found in 'Papier-Zeitung,' 1894, pp. 2099 & 2130.) A more efficient removal of the SO_3 and H_2SO_4 is effected by the apparatus of Némethy, G. P. 48285, of 1889, in which the gases from the burner pass through a large box containing iron borings &c. before entering the cooling-apparatus (comp. p. 283).

10. THE BURNER-GAS.

(1) *Composition of the Burner-gas from burning Brimstone.*

Atmospheric air contains, roughly speaking, 28 per cent. by volume of oxygen, and 79 per cent. nitrogen *: If it were possible to convert all the oxygen into sulphur dioxide, the volume would not be changed, since 1 mol. O_2 furnishes 1 mol. SO_2.

In the case of making sulphur dioxide for the manufacture of wood-pulp, we want to render it as free as possible from a surplus of oxygen. But for the manufacture of sulphuric acid we must introduce into the burner sufficient oxygen for later on forming SO_3, and a further excess practically necessary in the process. For the former object we must at once increase the oxygen by 50 per cent., as $2SO_2$ require O_2 for the formation of SO_3, and the theoretical maximum of SO_2 in the burner-gas would therefore be 14 per cent. together with 7 per cent. oxygen and 79 per cent. nitrogen. Practically we must have an excess of oxygen equal to 5 per cent. of the exit-gases from the system, together with 95 per cent. N.

If we call the unknown volume in the burner-gas of this excess oxygen $=x$, it must carry along $\frac{79}{21}x$ vols. N. To this are added

---

* Of course this item "nitrogen" comprises argon, helium, and all other indifferent gases recently discovered in atmospheric air. To simplify matters, we shall throughout this book omit the special mention of these gases, which in sulphuric-acid making play exactly the same inert part as elementary atmospheric nitrogen.

79 vols. N, entering along with the 21 vols. O required for forming 14 vols. of SO_2 and converting them into SO_3. The volume of the total N and of the excess oxygen required in practice for each 14 vols. of SO_2 introduced into the chambers thus amounts to

$$79+\frac{79}{21}x+x=79+\frac{100}{21}x.$$

x was stated to form 5 per cent. $=\frac{1}{20}$ of this volume.

We have thus the equation:

$$x=\tfrac{1}{20}\left(79+\frac{100}{21}x\right)=\frac{79}{20}+\frac{5}{21}x.$$

From this follows:

$$x-\frac{5}{21}x \text{ or } \frac{16}{21}x=\frac{79}{20},$$

$$x=\frac{79\times21}{20\times16}=5{\cdot}18 \text{ vols.};$$

that is, besides the theoretical quantities of gas mentioned above, another 5·18 vols. of oxygen, along with the corresponding $5{\cdot}18\times\frac{79}{21}=19{\cdot}50$ vols. of nitrogen, are necessary. The gaseous mixture formed in the sulphur-burner accordingly ought to contain upon each

14	vols. of	SO_2,
$7+5{\cdot}18=12{\cdot}18$	„	O, and
$79+19{\cdot}50=98{\cdot}50$	„	N.
124·68 vols.		

From this the following composition for 1 litre of this gaseous mixture is computed:—

0·1123	litre	SO_2
0·0977	„	O
0·7900	„	N
1·0000	„	

That is to say: *The normal quantity of* SO_2 *in burner-gas from brimstone-burners is* 11·23 *per cent. by volume.*

This normal quantity can be attained by proper care, but is frequently not reached.

(2) *Composition of the Burner-gas in burning Pyrites.*

The proportion of air required in this case differs very much from the preceding. We shall calculate this for pure iron disulphide. This body consists of 46·66 per cent. Fe and 53·33 per cent. S.

Although on burning dense pyrites sometimes the iron is not all oxidized up to Fe_2O_3, and a little magnetic oxide, Fe_3O_4, is formed, we must suppose the complete conversion of iron into Fe_2O_3 as the normal state to be aimed at for complete utilization of the sulphur. Consequently 2 mols. or 240 pts. of FeS_2 require 3 atoms = 48 pts. O for oxidizing the iron, and another 8 atoms = 128 pts. O for burning the S into SO_2. Altogether 11 atoms = 176 pts. oxygen are necessary for burning, and another 4 atoms of oxygen = 64 pts. for changing the formed 4 mols. = 256 pts. of SO_2 into SO_3. From this we calculate that for each thousand parts of FeS_2,

200	pts. oxygen	are required	for	oxidizing the iron,
$533\frac{1}{3}$	„	„	„	forming SO_2,
$266\frac{2}{3}$	„	„	„	oxidizing this to SO_3.
1000	„	in all.		

Now here also an excess of oxygen must be used, even larger than in the case of brimstone, which we will assume to amount to 6·4 per cent. by volume in the gas leaving the chambers. If we call the unknown volume of oxygen in excess to be introduced for each kilogram of S employed as FeS_2, x litre, the volume of nitrogen accompanying it is $\frac{79}{21}x$ litre. Both together and the 4933·3 litre N introduced along with the O requisite for combustion and formation of SO_3 form the gaseous mixture escaping at the end, the volume of which is therefore

$$4933{\cdot}3 + x + \frac{79}{21}x = 4933{\cdot}3 + \frac{100}{21}x.$$

As x is $\frac{6{\cdot}4}{100}$ of this volume, we have

$$x = \frac{6{\cdot}4}{100}\left(4933{\cdot}3 + \frac{100}{21}x\right),$$

$$x = 454{\cdot}1.$$

Accordingly for each kilogram of S burnt as FeS_2, apart from the theoretical 6244·7 lit. air, another 454·1 lit. oxygen along with $\frac{454\cdot1\times79}{21}=1708\cdot4$ nitrogen—that is, 2162·5 lit. air—altogether 8407·2 lit. air at 0° and 760 millims. pressure, have to be introduced.

Now each kilogram of free sulphur (brimstone) requires 6199 litres air at 0° and 760 millims.; consequently a certain quantity of sulphur, burnt as FeS_2, requires

$$\frac{8407\cdot2}{6199}=1\cdot356 \text{ times}$$

as much air as if burnt in the free state.

This is not quite the proportion of the gas *as it enters the chambers.* For on burning FeS_2 a portion of the oxygen remains behind with the iron, whilst on burning brimstone the whole quantity of air gets into the chambers, and at equal temperature and pressure retains its volume, since oxygen on combining with S to SO_2 does not change its volume.

The 8407·2 litres air entering the burner for each kilogram of sulphur burnt as FeS_2 furnished the following quantities of gas, calculated for 0° and 760 millims.:—

699·4 lit. SO_2 generated from the same volume of O,
349·7 „ O required for transforming SO_2 into SO_3,
454·1 „ O as excess,
4933·3 „ N accompanying the theoretically necessary oxygen,
1708·4 „ N „ „ excess of oxygen.

8144·9 lit. containing 699·4 lit. SO_2,
803·9 „ O,
6641·7 „ N.

For a certain quantity of sulphur, burnt as FeS_2, $\frac{8144\cdot9}{6199}$ times $=1\cdot314$ times as much gas must enter the chambers as if the sulphur were burnt in the free state.

Consequently, in the case of burning pyrites, 100 *volumes of the normal gaseous mixture on entering the chamber ought to consist of*

8·59 vol. SO_2,
9·87 „ O,
81·54 „ N.

In many factories the sulphur dioxide is much below 8·59 per cent., sometimes not above 6 per cent. of the volume of the gas. In that case so much less acid is made in the same chamber-space, unless the formation of sulphuric acid is increased by a larger consumption of nitre. We shall return to this subject in Chap. VII.

Sulphur Dioxide for manufacturing Calcium Bisulphite (*in the manufacture of wood-pulp, &c.*).—In this case the conditions are different from those just described. There is no question of having to provide the oxygen for forming H_2SO_4 from SO_2 and the excess of oxygen practically necessary in the lead chambers; and the formation of SO_3 in the burners should be avoided as much as possible. The operation should be conducted so as to exceed as little as possible the amount of oxygen demanded by the equation: $2\,FeS_2 + 11\,O = Fe_2O_3 + 4\,SO_2$, which corresponds to a theoretical maximum of 16 per cent. SO_2 by volume in the burner-gas. Practically, however, 11 per cent. should not be exceeded, because otherwise the burners get too hot, which causes the sublimation of sulphur and the formation of scoria in the burners.

Harpf (Wochenbl. für Papierfabr., Biberach, 1901, nos. 23, 25, & 27) gives some calculations referring to this special case, containing nothing of importance.

(3) *Composition of the gas from Blende-furnaces.*

For burner-gas from *zinc-blende* the following calculation has been made by Hasenclever (Chem. Ind. 1884, p. 79):—Zinc-blende (in the pure state), ZnS, consists of 63 parts Zn + 32 parts S. For burning it into $ZnO + SO_2$, $3 \times 16 = 48$ parts O are required, for converting the SO_2 into SO_3 another 16 O; therefore for 95 ZnS, containing 32 S, altogether 64 O. This means that each kilogram S in zinc-blende requires 2 kilograms O, or 1398·7 litres at 0° and 760 millims., together with 5258·0 litres nitrogen = 6656 litres air. In order to make allowance for the 6·4 volume per cent. of oxygen required to be in excess in the exit-gas, we find this by the formula:—

$$n = \frac{6{\cdot}4}{100}\left(5258 + \frac{100}{21}n\right),$$

$n =$ 484·0 litres oxygen, corresponding to
1820·7 „ nitrogen

2304·7 „ air.

Consequently the normal gaseous mixture in roasting 1 kilog. blende consists of :—

699·4 litres SO_2,
349·7 ,, O for forming SO_3,
484·0 ,, O in excess,
5288·0 ,, N entering with the theoretically necessary oxygen,
1820·7 ,, N ,, ,, excess oxygen,

8641·8 litres of gases.

This means that 100 volumes of the gas should contain :

8·12 vols. SO_2
9·69 ,, O
82·19 ,, N.

According to information received in 1902 the blende-gases contain only exceptionally less than 6 per cent. SO_2 ; ordinarily 6 to 7·5 per cent. SO_2 apart from SO_3 (see below).

So far, as we see from Hasenclever's calculation, theory would show that the strongest obtainable burner-gas from blende is not much inferior to that obtainable from pyrites (p. 400). But apart from the fact that here, as well as in the case of pyrites and to some extent even of brimstone, the theoretical figures are undoubtedly interfered with by the formation of sulphuric anhydride, there is, at least with all the older blende-furnaces, a far more potent reason why the practical percentage of SO_2 in blende-gases should be far below the theoretical one. Seeing that in those furnaces only $\frac{1}{2}$ or at most $\frac{2}{3}$ of the sulphur was liberated as SO_2 [and SO_3], that the other $\frac{1}{2}$ or $\frac{1}{3}$ remained behind in the state of $ZnSO_4$, and that the nitrogen corresponding to the four atoms of oxygen contained in $ZnSO_4$ dilutes the burner-gas, it is easily understood why formerly it was considered *good* work if blende-gases contained 5 or at most 6 per cent. of SO_2. The modern furnaces (p. 360 *et seq.*) undoubtedly yield better gases, not much inferior to the burner-gas from pyrites.

(4) *Sulphuric anhydride in Burner-gas.*

In the pyrites-burner, besides sulphur dioxide, there is always sulphuric anhydride formed during the burning. This fact has long been known, and was explained in 1852 by Woehler and Mahla, and again in 1856 by Plattner ('Die metallurgischen Röstprocesse') after many experiments, in this way—that many substances, one of which (ferric oxide) is present in large quantity in the pyrites-burner, dispose sulphur dioxide to combine with the oxygen of the air to form sulphuric anhydride. We have already seen, and in Chapter XI. the subject is fully detailed, that this reaction can be used for the production of sulphuric anhydride itself. Another plausible explanation is, that in the cooler parts of the pyrites-burners sulphates of iron are formed, which in the hotter parts again split up into Fe_2O_3 and SO_3. This explanation, however, is not sufficient for Fortmann's experiments (Dingl. Journ. clxxxvii. p. 155), according to which the whole of the fumes of anhydride appear the moment the pyrites take fire. Scheurer-Kestner (Bull. Soc. Chim. 1875, xxiii. p. 437) explained the matter from the well-known fact that ferric oxide can act as an oxidizing agent by successively giving up and absorbing oxygen. It is, however, established that even on burning pure sulphur a little anhydride is formed, as we shall see.

In Fortmann's experiments, made on a small scale, on burning pyrites far more SO_3 than SO_2 was formed, viz. in one experiment 4 times as much, in another as 5 : 3. His results were evidently altogether wrong, in consequence of a faulty analytical method. Scheurer-Kestner (*loc. cit.*) only found 2 or 3 per cent. of all the SO_2 converted into SO_3, but a larger deficiency of oxygen in the gas than corresponds to this amount; and the later discussion between Bode (Dingl. Journ. ccxviii. p. 325) and Scheurer-Kestner (ib. ccxix. p. 512) did not clear up the matter.

In order to decide the question of the formation of SO_3 on burning pyrites by more exact methods than those hitherto used, especially by Fortmann, I made, together with Salathe, a series of experiments (Deutsch. chem. Ges. Ber. x. p. 1824). It was found that SO_2 cannot, as Scheurer-Kestner had supposed, be absorbed and estimated by barium chloride, because even chemically pure SO_2 with $BaCl_2$ in the presence of O or atmospheric air at once gives a precipitate of $BaSO_4$. Check tests proved that exact results were obtained by conducting the gas through an excess of standard iodine solution, retitrating the latter by sodium arsenite, and estimating the total sulphuric acid formed in another portion of the liquid by precipitation with $BaCl_2$. By retitration the quantity of SO_2 absorbed was found, and by subtracting this from the total sulphuric acid that of the SO_3 was obtained. Two experiments with burning Spanish cupreous pyrites, containing 48·62 per cent. of sulphur, in a glass tube in a current of air gave

	I.	II.
Sulphur obtained as SO_2	88·02	88·78 p. c.
„ „ SO_3	5·80	6·05 „
„ in the residue.........	3·43	5·17 „
„ lost	2·75	

Of the sulphur of the burner-gas itself there were present

	I.	II.
As SO_2	93·83	93·63 p. c.
„ SO_3	6·17	6·37 „

Two other experiments were made in this way:—In the glass tube 50 grams of cinders from the same pyrites, in pieces about the size of a pea, were completely freed from sulphur by ignition, and fresh pyrites burnt as before, the gas passing through the cinders. Found:—

	III.	IV.
Surphur as SO_2	79·25	76·90 p. c.
„ SO_3	16·02	16·84 „
Residue and loss	4·73	6·26 „

Of the sulphur of the burner-gas itself there were present:—

	III.	IV.
As SO_2	83·18	82·00 p. c.
„ SO_3	16·82	18·00 „

On the large scale the formation of SO_3 will hardly be as much as in the last two experiments, because in the burners the gas passes through much less ignited ferric oxide than in our experiments.

By later experiments in my laboratory (Chemiker-Zeitung, 1883, p. 29) it was found that in roasting pyrites by itself 5·05 per cent., when passing the gases through a layer of red-hot pyrites-cinders 15·8 per cent. of the total sulphur reappeared as SO_3, which entirely confirms the above results. On burning *brimstone* it was found that even here 2·48–2·80 per cent. of the sulphur was converted into SO_3; and this quantity was increased to 9·5–13·1 per cent. if the gases were passed through red-hot pyrites-cinders.

Hempel (Ber. d. deutsch. chem. Ges. 1890, p. 1455) found that, on burning brimstone in oxygen at the ordinary atmospheric pressure, about 2 per cent. of it was converted into SO_3 (which agrees with my results, as given above); but when effecting the combustion under a pressure of 40 or 50 atmospheres, about half of the sulphur was converted into SO_3.

Further experiments were made by Scheurer-Kestner (Bull. Soc. Chim. xliii. p. 9, xliv. p. 98) with the gases from pyrites-kilns as given off in actual manufacturing. We quote here a series of his results, obtained with samples of burner-gas taken at various times—A, from a lump-burner; B, from a Malétra dust-burner.

	Volume per cent. of SO_2.	Sulphur converted into SO_3 per cent. of total S.	
A. *Lump-burner.*	7·3	2·8	Average 3·1
	7·5	5·8	
	6·5	1·2	
	6·6	1·0	
	8·3	0·0	
	9·9	2·8	
	6·2	8·4	
B. *Dust-burner.*	8·2	3·0	Average 3·5
	9·0	6·8	
	7·6	0·4	
	11·3	0·8	
	7·7	1·0	
	8·7	2·5	
	8·7	9·3	
	7·6	4·1	

The quantity of SO_3 formed is here found to be very irregular, varying from 0 to 9·3 per cent. of the SO_2; the average is decidedly less than in our laboratory experiments with pyrites.

F. Fischer (Dingl. Journ. cclviii. p. 28) obtained the following results, which at the same time give an idea of the difference in the composition of the gases on the various shelves of a Malétra dust-burner:—

	SO_2 per cent.	SO_3 per cent.	O per cent.
A. *First test* (shelf-burner).			
Second shelf from below	0·96	0·44	18·4
Fourth „ „	1·52	0·68	16·6
Sixth „ „	3·81	0·97	12·5
Main flue	8·26	1·34	5·9
„ „	7·53	1·27	7·5
B. *Second test* (shelf-burner).			
Sixth shelf from below	8·43	3·17	3·9
„ „	4·92	0·68	10·7
Second shelf from below	2·48	1·42	14·8
Fourth „ „	2·62	0·78	16·0
Main flue	5·80	0·65	10·6
C. *Lump-burner* up to	9·3	2·1	5·0

These tests were made by an expeditious method which cannot compete as to accuracy with that employed by me or by Scheurer-Kestner. The much larger quantity of SO_3 in proportion to SO_2 is perhaps explicable in this way *.

Blende-roasting gases, when tested by my method at the Rhenania works at Stolberg, yielded up to 25 per cent. of the total S as SO_3.

If the burner-gases are not passed hot into a Glover tower, but are cooled in the old way, most of the SO_3 condenses in the shape of sulphuric acid, more than enough water for this purpose being contained in the air and the pyrites. Where the gases go into a Glover tower, this, of course, retains all the SO_3 previously formed, also in the shape of SO_2H_4 (Scheurer-Kestner, *loc. cit.*). We shall further on consider this fact in detail when speaking of the Glover tower and the formation of sulphuric acid generally.

The constant presence of sulphuric anhydride in various proportions in the burner-gas is, of course, a source of inaccuracy in the testing process according to Reich (see below), which indicates only the sulphur dioxide, as we shall see later on; it causes, moreover, a deficiency of oxygen and an excess of nitrogen in the composition of the gases. Hitherto no satisfactory relation has been found between the amount of SO_2, SO_3, O, and N in the many analyses of burner-gases, as is apparent from the disputes between Scheurer-Kestner and Bode (*vide suprà* p. 403; comp.

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* Harpf (Dingler's Journ. ccci. part 2) has grossly misinterpreted Scheurer-Kestner's results, as shown by me, *ibid.* part 4.

also Ber. d. deutsch. Chem. Ges. vii. p. 1665), as well as from Fischer's tests just quoted.

(5) *Actual Percentage of Sulphur Dioxide in Burner-gas.*

Another source of dilution of the burner-gas, likewise not traceable quantitatively, is this—that the burnt ore does not contain pure Fe_2O_3, but sulphates of iron, which must always retain more oxygen than Fe_3O_3, and the nitrogen corresponding to this excess of oxygen must be found in the burner-gas. On the other hand, a little nitrogen will have to be deducted if in the burnt ore FeS is present; but this amounts to very little indeed.

Lastly, in the factories working with nitrate of soda decomposed immediately behind the burners, the dilution of gas caused thereby must be accounted for. The calculated density of NO_3H is 2·17823; we need only take this into account, as the NO_3H forms the largest portion of the gas given off by the nitre mixture. It differs so little from that of SO_2 (viz. 2·21126), that, looking at the small quantities in question, we can take the two as equal without any sensible error. Now in normal working order, and using a Gay-Lussac tower, certainly not above 5 per cent. of nitre on the burnt sulphur is consumed (corresponding to 3·7 per cent. of NO_3H), or 1·85 upon the SO_2. Thus a gaseous mixture which, without the nitric acid, contains 8·59 per cent. of SO_2, contains besides $\frac{1{\cdot}85 \times 8{\cdot}59}{100} =$ nitric acid vapour, which increases its volume to 100·1589, and diminishes the percentage of SO_2 in the total volume to 8·576—a diminution too slight to be traceable by analysis. Even if the nitric acid is not calculated as such, but as NO_2 or N_2O_3, it has no sensible influence upon the analyses, even if the sample of gas is taken in a place where the nitrous vapours coming from the Gay-Lussac tower have already entered into the process.

Still all the above-mentioned causes unite in somewhat diminishing the percentage of SO_2 in the burner-gas: so that the percentages stated above:—

11·23 per cent. by volume in burning sulphur,
8·59 „ „ „ pyrites,

must be looked upon as the *maximum*, which in practice can only be approached, but hardly ever reached, and which ought never to be exceeded.

If the sulphur dioxide in the burner-gas be estimated, this will sufficiently test the style of burning, since the oxygen of the gas must necessarily be in inverse proportion to its sulphur dioxide—although not exactly, as the sulphuric anhydride comes into play. In practice, usually from 11 to 13 per cent. of oxygen is found in good burner-gas.

The innumerable observations made upon the percentage of burner-gas in chemical works during recent years have proved that with very good pyrites the above maximum figures can be very nearly approached, whilst with other ores, badly burning or containing unfavourable metallic sulphides, only 7 to 7½ per cent. SO_2 in the burner-gas is attained (*e. g.* Büchner, Dingl. Journ. ccxv. p. 557). Of course, looking at the difficulty of keeping the evolution of gas exactly equal, the different observations made in the course of a day will frequently yield less than the above figures (*e. g.* Scheurer-Kestner, in Dingl. Journ. ccxix. p. 117, in one day found 6·5, 6·5, 6·0, 8·0, 9·0, 8·7; even greater differences occur in his tests quoted *supra*, p. 405); and they only signify the *average* percentage of the burner-gas. As a *minimum*, below which the gas of real pyrites ought never to fall, 6—as ordinary average, 7 to 8 per cent. SO_2 by volume can be assumed. If less is found, the draught should be cut off; if more, more air should be admitted.

Crowder (J. Soc. Chem. Ind. 1891, p. 298) quotes the following observations on the volume-percentage of burner-gas (details in the original; no account is taken of the SO_3 present):—

	SO_2.	O.
Lump-kilns......................from	4·97 to 6·33	9·60 to 11·21
Old dust-kilns (shelf-burners) „	6·03 „ 7·02	9·10 „ 10·00
Ditto, another ore.............. „	6·34 „ 7·43	7·78 „ 8·82
New dust-kilns .... „	4·86 „ 7·03	8·98 „ 10·68

The temperature of the gas, where it enters the Glover tower, in the case of lump-burners is between the melting-points of zinc (412° C.) and antimony (432°). The gas from dust-burners, which has first to traverse a series of dust-chambers, is generally hot enough to melt lead (=326°), but it is sometimes rather less.

In the case of the Rhenania blende-furnaces (p. 361) the gases arrive at the Glover tower above 300° C., sometimes up to 400° C.

All the above calculations refer only to pyrites proper—that is, containing merely a few per cent. of other metallic sulphides.

If the latter have to be roasted by themselves (for instance, preparatory to their metallurgical utilization), only poor gas can be obtained, partly because more sulphates remain in the residue, for which the corresponding nitrogen is found in the gas, partly because they must be roasted altogether with a larger excess of air.

Bode states ('Gloverthurm,' p. 88) that at Oker poor ores with 27 per cent. sulphur, of which only 22 per cent. was combined with iron, the remainder being present as blende and barium sulphate, yielded gas with 5·5 per cent. SO_2. Lead-matte yields gas with 5 to 5·5 per cent.; coarse copper metal (with 34 per cent. Cu, 28 per cent. Fe, and 28 per cent. S), 5·5 per cent. SO_2.

According to Wunderlich (Zeitschr. f. d. chem. Grossgew. i. p. 74), the gas at Oker contains 5 to 7 per cent. SO_2; its temperature in the case of ores rich in sulphur reaches 360°, in the case of poorer ores about 230°.

Attention must be drawn to a circumstance frequently overlooked in analyses—that for technical purposes very rarely a reduction of the volumes of gases to 0° and 760 mms. is effected. This matters less in ordinary gas-analysis than in tests like that of Reich, where the gases are compared with a fixed quantity of SO_2 assumed to be at 0° and 760 mms. This causes most tests made by Reich's method to indicate less than the real percentage of SO_2 present.

Usually 4 per cent. SO_2 in the gases entering the chambers is considered the minimum at which it is possible to make sulphuric acid without actually losing money by the process. Locally, of course, this may be modified to some little extent. At Freiberg 4 to 3½ per cent. SO_2 is stated as the minimum at which the manufacture of sulphuric acid can be carried on without pecuniary loss. The average at those works, where a great variety of poor ores, all arsenical, and "matte" is roasted, preparatory to the smelting process, is from 5 to 7 per cent. SO_2 in the burner-gas.

(6) *Comparison of Brimstone and Pyrites as Material for Sulphuric-acid-making.*

We have seen above that the burner-gas from brimstone is richer than that from pyrites in the proportion of 1 to 1·314; that is to say, under equal conditions, the gas generated in burning pyrites occupies 1·314 times as much space as if the same quantity of sulphur had been employed as brimstone. From this it directly follows that the gas will also require much more chamber-space; thus, for an equal production of sulphuric acid, the chambers must be about one third larger if working with pyrites than if working with brimstone. Usually it is assumed that the consumption of nitre has to be increased in a similar ratio; this, however, is not the case, as a properly constructed Gay-Lussac tower retains almost the whole of the nitre-gas, and the excess volume of air is not of great importance. At the present day, indeed, in well-managed works, less nitre is used with pyrites than has ever been used with brimstone.

Leaving the nitre out of consideration, the advantages of using brimstone are:—a somewhat higher yield of acid (see Chap. X.); rather less cost of plant, and less trouble with the burners if any thing goes wrong; and, above all, much greater purity of the sulphuric acid, especially from iron and arsenic (this is important only for sale acid, not for use in manure-works, alkali-works, &c.). If brimstone could be had at the same price as the sulphur in pyrites, nobody would hesitate for a moment to employ the former; and even a moderately higher price would not deter from this; but where the pyrites-sulphur, as is the case in most industrial countries, only costs half the price of brimstone, or even less, the latter cannot be employed, except for *pure* acid; and even this, when the difference in price is very large, can be more cheaply made from pyrites than from brimstone.

Owing to this cause, the manufacture of brimstone-acid in Europe is confined to small factories which make specially pure acid for bleach-works, for manufacturing articles of food, &c. A somewhat considerable number of such factories still exist in England, whilst very few are found in other European countries. But it should be noticed that sometimes acid is sold in England as "brimstone-acid" which is in reality made from pyrites and purified from arsenic, or else acid made from spent oxide of gas-works, which is also practically free from arsenic.

In America formerly all sulphuric acid was made from Sicilian brimstone; but the notes given above (p. 58) as to the consumption of pyrites in America show that this is rapidly gaining ground.

It is frequently asserted that sulphuric-acid chambers worked with brimstone last very much longer (up to three times) than with pyrites. It is not impossible that there is *some* difference in this respect; but even this is not certain, and at all events the difference in the duration of the chambers is nothing like so great as was formerly supposed, and forms no item in a comparison of costs (comp. Chap. V.).

(7) *The Quantitative Estimation of Sulphur Dioxide in Burner-gas.*

This is usually effected by Reich's process, which consists in aspirating the gas through a measured quantity of a solution of iodine, to which a little starch has been added. This is carried on till the blue colour of the solution disappears; the amount of gas aspirated in proportion to the constant quantity of iodine employed admits of calculating the percentage of SO_2 in the gas.

The reaction taking place is as follows:

$$2\,I + SO_2 + 2\,H_2O = 2\,HI + H_2SO_4.$$

The operation is carried on with the apparatus shown in fig. 137. A is a wide-mouthed bottle of about 200 or 300 c.c. capacity, provided with a three-times perforated india-rubber cork. Through one perforation passes the glass tube *a*, which, by means of the elastic tube *b*, serves for introducing the gas; for this purpose a hole is drilled in some convenient part of the burner-pipe, and the india-rubber cork *c* exactly fitted into it. The second, somewhat wider perforation is closed by the small plug *d*; through the third the elbow tube *e* passes, which is connected with the corresponding tube *f* of the bottle B, holding 2 or 3 litres. The latter serves as an aspirator—the glass tube *g*, reaching to its bottom, being continued into an elastic tube *h*, closed by the pinch-cock *i*, the whole when once filled serving as a siphon. The graduated cylinder, C, holds 250 cub. centims.

When the sulphur dioxide in any gaseous mixture has to be estimated, the cork *c* is inserted into a hole of the pipe conveying the gas.

The vessel A is filled up to about half of its capacity, through *d*, with water; and B is filled almost entirely. A small quantity (usually 10 c.c.) of standard iodine solution (12·65 grams I in 1 litre of water) is added to the water in A, along with a little starch, by which the water assumes an intensely blue colour. The pinch-cock on the elastic tube *b* is shut so that no air can enter into A; *i* is opened, so that water runs out until the air in A and B is so far expanded that the column of water in B is supported. The water then ceases to run, provided that everything closes air-tight; if not, the water will continue to run. When the apparatus has been thus tested, *i* is shut and *b* opened; then *i* is opened so that the water runs out slowly, the gas to be tested entering through *a* in single bubbles and rising through the coloured water. As soon as the SO_2 contained in the gas gets into the water, it converts the free iodine into hydriodic acid; and after a certain time the liquid will be decolorized, which at last happens very suddenly and can be very accurately observed. Directly this happens, the cock *i* is closed. By this preliminary operation the whole of the inlet-tube is filled with the gas to be tested.

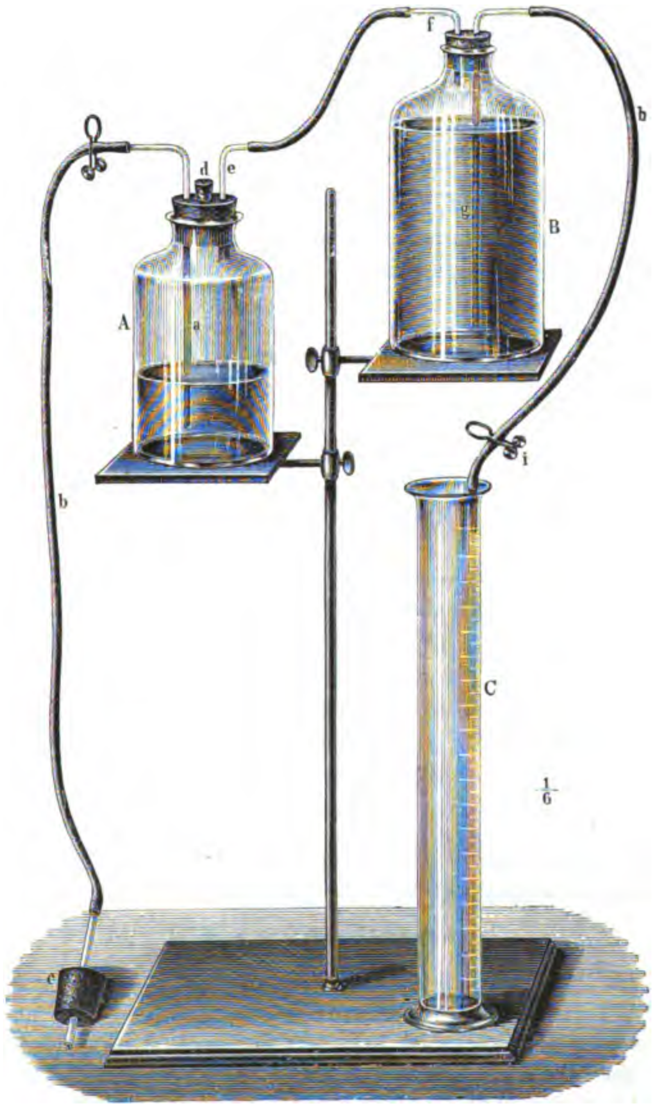
Now *d* is opened, and a measured volume (say, *n* cub. centims.) of standard iodine solution is put into the vessel A, by which, of course, a blue colour is again produced; *d* is closed again; *i* is cautiously opened, and water is run out till the liquid in *a*, which, on opening *d*, had risen to the level of the outer liquid, has been depressed to the point of the tube, in order to expand the gas in A up to the degree of pressure at which the following observation is made; then *i* is quickly shut, all the water that runs out is poured away, and the empty graduated vessel C is put back into its place. Now *i* is opened, and, by the running-out of the water, gas is slowly aspirated through A, till the liquid is decolorized again, whereupon *i* is closed, and the volume of the water run out into the graduated cylinder is measured. We will call it *m* cub. centims.. In this process no sulphur dioxide escapes unabsorbed if the bottle A is constantly shaken; it is best to do this with one hand, holding the pinch-cock *i* open with the other hand, and letting this go the moment the colour has vanished, or even when it is but faint, as it generally disappears on shaking a little longer.

It is advisable to add to the iodine solution a little sodium bicarbonate, which will facilitate the absorption of SO_2 (C. Winkler).

If a second testing is to be made, without any further alteration a fresh quantity of iodine solution can be put in and the process recommenced. When this has been repeated a few times, the decolorized liquid in A, after a short time, again turns blue, because then its percentage of HI has become so large that it decomposes on standing and liberates iodine. This liquid must then be poured away, and replaced by fresh water and a little starch solution.

The calculation of the result is as follows :—The *n* cub. centims. of iodine solution, provided it contains 12·65 grams per litre, by

Fig. 137.



its decolorization shows 0·0032 gram SO_2, which, at 0° C. and a barometrical pressure of 760 millims., occupies a volume of $1{\cdot}114 \times n$ cub. centims. If the barometer shows b millims., and the thermometer t° C., and the difference of water-level in the aspirator is $=h$ millims., equal to $\frac{h}{13\cdot6}$ millims. of mercury, the exact volume of $0\cdot0032 \times n$ gram SO_2 is

$$1\cdot114 \times n \times \frac{760}{b-\frac{h}{13\cdot6}} \times (1+0\cdot003665\,t) \text{ cub. centims.}$$

As the water run out, and thus also the gas aspirated through A, amounts to m cub. centims., the volume of the aspirated gaseous mixture, before the absorption of the SO_2 contained therein, must have been

$$m+1\cdot114 \times n \times \frac{760}{b-\frac{h}{13\cdot6}} \times (1+0\cdot003665 \times t) \text{ cub. centims.,}$$

and the percentage of SO_2 in volumes of the gaseous mixture

$$\frac{100 \times 1\cdot114 \times n \times \frac{760}{b-\frac{h}{13\cdot6}} \times (1+0\cdot003665 \times t)}{m+1\cdot114 \times n \times \frac{760}{b-\frac{h}{13\cdot6}} \times (1+0\cdot003665 \times t)}.$$

In many cases a correction for the barometrical and thermometrical changes will not be required; and the formula is then simply

$$\frac{111\cdot4 \times n}{m+1\cdot114 \times n} \text{ per cent. } SO_2.$$

If the percentage of SO_2 in the gas is very small, and thus m very large in proportion to n, the formula may be simplified into

$$\frac{111\cdot4 \times}{m}.$$

If 10 cub. centims. of a decinormal iodine solution (=12·65 grams in 1000 cub. centims.) have been put into A, this quantity, according to the above-given formula, will correspond to 0·032 gram, or 11·14 cub. centims. SO_2, at 0° C. and 760 millims.; and this number need only be multiplied by 100, and divided by the number of cub. centims. of water collected in C, *plus* 11, in order to find the percentage of SO_2 in the gas. The barometrical and thermometrical corrections are in this case, of course, neglected. The subjoined Table will save this calculation. On employing 10 cub. centims. of decinormal iodine solution, the following number of cub. centims. collected in the graduated cylinder, C, show :—

Cub. centims.	Volume percentage of SO_2.
82	12·0
86	11·5
90	11·0
95	10·5
100	10·0
106	9·5
113	9·0
120	8·5
128	8·0
138	7·5
148	7·0
160	6·5
175	6·0
192	5·5
212	5·0

Even if the gas to be examined is taken at a point where it is already mixed with nitre gas, this will not exercise any practically important influence upon the result. We have already seen that, in ordinary work, for each 100 parts of SO_2 only 1·85 NHO_3, or its equivalent as N_2O_3 or NO_2, exists in the gas. In such dilute aqueous solutions as come into question here nitric acid hardly at all oxidizes sulphurous acid; this, however, is done by nitrous and hyponitric acids. Even if we assume that only NO_2 is formed (which is going much too far), this could at most oxidize its equivalent in SO_2, according to the formula

$$NO_2 + H_2O + SO_2 = SO_4H_2 + NO.$$

46 NO_2 thus oxidizes 64 SO_3, or 1·35 NO_2 (the equivalent of 1·85 NO_3H) only 1·88 SO_2; in other words, in the worst case, never happening in practical work, of 100 parts.SO_2 1·88 part would be oxidized by nitrogen acids instead of iodine. Even this maximum error would, say, at 10 per cent., only amount to a deficiency of 0·188 per cent.; but this is certainly reckoning it much too high.

(8) *Lunge's Test for total Acids in the Burner-gas.*

Considering the inaccuracy peculiar to Reich's test, owing to the constant presence of sulphuric anhydride in the burner-gas (comp. *supra*, p. 402 *et seq.*), the question arises whether it would not be better to substitute for it a test showing the *total acidity* of the burner-gases. There is no difficulty in doing this, either by the method indicated for testing the exit-gases, or in a more expeditious way by employing in the apparatus (fig. 138) a caustic-soda solution tinged red by phenolphthalein (litmus is not suitable in this case, nor is methyl-orange, which acts differently upon sulphurous and sulphuric acid, comp. p. 160). I have shown this method to be quite practicable and accurate, and it is carried out at many works for the regular control of the process. A decinormal solution of caustic soda is employed, of which 10 c.c. are tinged red with phenolphthalein and diluted to about 100 or 200 c.c. The gas is aspirated through it slowly, exactly as in Reich's test, with continuous shaking. Especially towards the end the shaking must be continued for a while (say ½ minute) each time after aspirating a few c.c. of gas through the liquid, till the colour has been completely discharged, which is best ascertained by putting a white piece of paper or the like under-

Fig. 138.

neath the bottle. The calculation is made exactly as with the iodine test, counting all the acids as SO_2. A large number of practical tests made in this manner have shown that the percentage of total acids calculated as SO_2 is always larger than the figures found by the iodine test, owing to the presence of SO_3, and that the results of the former test agree with those of gravimetrical estimations.

The absorption-bottle used by me differs from Reich's in having an inlet-tube for the gas, closed at the bottom, and perforated with many pin-holes, through which the gas rises in many minute bubbles, instead of one large bubble, as shown in fig. 138. Experience proves this to be greatly superior to fig. 137.

The otherwise excellent absorbing-bottle described in No. 34 of the Alkali Inspectors' Reports, p. 22, is not available in this case, as it contains india-rubber rings, which act upon iodine.

(9) *Estimation of Oxygen in Burner- and Chamber-gases.*

Although burner-gas is not generally tested for oxygen, this test being reserved for the exit-gases, we will here describe the methods employed for estimating oxygen in any of the gases occurring in the manufacture of sulphuric acid.

Oxygen is for technical purposes always estimated by means of an absorbent, observing the contraction of volume produced. Some of these absorbents are not now employed, as nitric oxide (used by Priestley and recently by Scheurer-Kestner, Compt. Rend. lxviii. p. 608; also lately recommended by Wanklyn), ferrous hydrate (Vogt, Dingl. Journ. ccx. p. 103), and others. Cuprous chloride in ammoniacal solution may be employed for absorbing oxygen, but it has no advantages over pyrogallol or phosphorus, and several drawbacks, so that it cannot be recommended. The choice really lies between the two agents just mentioned.

Of these *pyrogallol* must be used in an alkaline solution, and it acts very promptly indeed. Its use for this purpose was proposed by Chevreul as early as 1820, but it became general only through Liebig many years after. It is true that this reagent in the presence of pure oxygen forms some carbon monoxide (Crace Calvert, Proc. Manch. Lit. & Phil. Soc. 1863, p. 184); but this never happens with gaseous mixtures containing no more oxygen than atmospheric air (Poleck, Zeitschr. f. analyt. Chemie, 1869,

p. 451). It is therefore altogether reliable in the present case, and is very much employed. Its drawback is that the solution (25 grm. potassium hydrate and 10 grm. pyrogallol to 400 c.c. water) gradually thickens and becomes useless long before this somewhat expensive reagent has been used up.

Phosphorus is one of the oldest absorbents for oxygen, and it has again come into use, since the manner of employing it has been properly studied, and as it is now found in trade in very thin sticks, offering a great surface. Of course it must be kept under water, and must be exposed only to the gas to be analyzed. It acts only at a temperature of at least 16°, better a little above; this is the first condition to be observed in its use, but it is easy to attain if the apparatus is kept in a somewhat warm place (near an acid-chamber). The action of phosphorus on oxygen is interfered with by traces of tarry matters and the like; but such do not occur in chamber-gas. As it is, the gases, both for the pyrogallol and the phosphorus test, are often previously washed and freed from acids by passing them through a solution of caustic potash; but there is generally no great error made by omitting this treatment. The action of the oxygen on the phosphorus is at once indicated by the formation of a white cloud, and it is necessary to wait a few minutes till that cloud has completely disappeared, when the absorption of oxygen will be complete. Once charged, such an apparatus may serve for hundreds of tests, but it should be kept from daylight.

The apparatus employed for estimating oxygen in gaseous mixtures may be of various descriptions. Those most used are Orsat's apparatus (comp. Lunge and Hurter's Alkali-Maker's Pocket-Book, p. 74, and Winkler-Lunge's Technical Gas-Analysis, 2nd edition, p. 87), Lindemann's apparatus (ibid. p. 92), and M. Liebig's apparatus (Dingl. Journ. ccvii. p. 37, and ccxxxiii. p. 396); Younger's apparatus (J. Soc. Chem. Ind. 1887, p. 348) is a slight modification of the latter. The two former can be used for phosphorus or pyrogallol, the latter for pyrogallol only.

Of course Hempel's, Bunte's, or any other apparatus for general technical gas-analysis may be employed as well.

Instead of taking only single samples of the escaping gas, it is advisable, along with these, to collect an average sample (say, for 24 hours) by aspirating a certain quantity (say, about 50 litres) by means of a large aspirator with the outlet-cock very slightly opened. Owing to the slowness of the aspiration, the gas standing over the water in the aspirator will be thoroughly mixed up, and by taking a sample from the aspirator the *average* percentage of oxygen can be estimated with some degree of accuracy. We shall treat this matter more in detail in the 7th Chapter, when describing the testing of the exit-gases.

(10) *Estimation of the Oxides and Acids of Nitrogen in Gaseous Mixtures.*

Burner-gas will contain the above acids if the "potting" has been done either within or close to the burners, as is usual in England. The acids and oxides of nitrogen are, however, but exceptionally estimated in burner-gas, and not very often even in chamber-gas; the latter is not indispensable, because the colour of the chamber-gas on the one hand, and the testing of the "drops" on the other, which we shall describe in the 5th Chapter, are sufficient for guiding the manufacturer in his work.

In well-conducted works, however, the chamber-exits are tested not merely for total acidity, but also for nitrogen acids separately. For this purpose the prescriptions formulated in 1878 by the British Alkali-Makers' Association may be observed, which we shall give in detail later on (Chap. VII.). These do not extend to nitric oxide, but we shall see that it is easy to estimate this at the same time. In this place we shall give a short outline of the methods employed by Lunge and Naef for their extended experimental investigation of the vitriol-chamber process ('Chemische Industrie,' 1884, p. 5) for *estimating nitrogen oxides and sulphur dioxide at the same time.* The pipe bringing the gas from the chambers is continued into a Y-pipe, both branches of which are connected with sets of absorbing-tubes. One branch is connected with three U-tubes containing concentrated pure sulphuric acid (for retaining N_2O_3 and N_2O_4) and a fourth tube containing an acidulated solution of potassium permanganate (for retaining NO). The other branch of the Y-pipe first leads into a long glass tube filled with cotton-wool or glass-wool, where any drops of mechanically carried-over sulphuric acid are retained, and then into two U-tubes containing pure caustic-soda solution (for estimating SO_2). At the end of both sets of tubes there is an aspirator, consisting of a large glass bottle, holding about 20 litres, divided into single litres, with a tap or tap-siphon leading into a similar bottle, so that the quantity of water run out indicates the quantity of gas passed through each set of tubes. The gas remaining in the aspirators is tested for *oxygen* by absorption; *nitrogen* by difference. *Sulphur dioxide* is found by oxidizing the caustic-soda solution with bromine-water and precipitating the sulphuric acid formed by barium chloride. In the sulphuric acid *nitrogen trioxide* and *tetroxide* are estimated in the way indicated in Chapter III. (p. 253 *et seq.*), by testing both with permanganate and with the nitrometer. The tube filled with potassium permanganate must have retained the *nitric oxide,* which is found by adding titrated ferrous sulphate solution and re-titrating with permanganate. Where the quantity of SO_2 in the gas is considerable, this method cannot be employed; in this case it is not possible to separate the N_2O_3 and N_2O_4, and the method otherwise used for the chamber-exits must be employed (Chapter VII.).

Nitrous oxide has never yet been actually proved to exist in chamber-gases; but it probably does occur there in very slight quantities. The former methods of its detection and estimation were very inadequate and failed entirely in the presence of other nitrogen oxides. It may be possible to apply the method proposed by Knorre (Berl. Ber. xxxiii. p. 2136), viz. burning with excess of hydrogen in a Drehschmidt's platinum capillary (comp. Winkler-Lunge's Technical Gas-Analysis, 2nd edition, p. 162), or else Pollak's method (described in his inaugural dissertation, Prag, 1902, p. 52, and in Treadwell's 'Lehrbuch der analyt. Chemie,' 2nd ed. ii. p. 538) of burning in a bright red-hot Drehschmidt's capillary with pure carbon monoxide, measuring the contraction and estimating the CO_2 formed. The contraction in burning for NO is $\frac{NO}{2}$; for N_2O there is no contraction at all; the volume of the absorbed CO_2 is equal to $NO + N_2O$. Hence the volume of N_2O is obtained by deducting twice the volume of the first contraction from the volume of CO_2 found. This is made clear by the following equations:—

$$2 \text{ vol. } NO + 2 \text{ vol. } CO = 1 \text{ vol. } N_2 + 2 \text{ vol. } CO_2.$$

$$1 \text{ vol. } N_2O + 1 \text{ vol. } CO = 1 \text{ vol. } N_2 + 1 \text{ vol. } CO_2.$$

CHAPTER V.

CONSTRUCTION OF THE LEAD CHAMBERS.

We have already seen, p. 8 *et seq.*, through how many stages the construction of that apparatus has gone in which formerly all sulphuric acid, other than fuming oil of vitriol, was made and up to now is still made for the most part, viz. the *lead chamber*. The reader already knows that sulphuric acid is formed by the oxygen of the air being transferred to sulphur dioxide through the intervention of the acids of nitrogen and with the aid of a molecule of water, thus :

$$SO_2+O+H_2O=SO_4H_2.$$

All the substances entering into the process are in the state of a gas or vapour, except the water which is sometimes introduced as a spray or mist. The reaction takes a certain time, as the nitrogen compounds which serve as carriers of oxygen have to be frequently reduced and reoxidized, and as the gases and liquids are only gradually mixed so intimately that they can actually enter into reaction. There must therefore be a space provided in which large quantities of gas can remain for some time. According to the calculations given on pp. 397 and 399, for each kilogram of sulphur in the state of brimstone 6199, or in the state of pyrites 8145 litres of gas, reduced to 0° and 760 millims. pressure, must enter into reaction; and these figures are a good deal increased by the higher temperature, the steam, &c. In order to harbour such vast quantities of gas, very large spaces must be provided. Since the strongest acids have to be dealt with, both in the liquid and the gaseous form, most materials otherwise used in building are out of the question; and since, of those suitable, glass, earthenware, &c. are excluded by the large size of the apparatus, practically only *one* material remains which is sufficiently cheap and suitable for the purpose, viz. *lead*. The disadvantages of this metal, such as its great weight, its softness and lack of rigidity, its easy fusibility, its comparatively high price, cannot outweigh the advantages which none of the base metals share with it for our purpose, viz.:—the great chemical resistance to the acid gases and liquids; its ductility, which permits rolling it into large sheets; its extraordinary pliability and toughness, in consequence of which it can easily be shaped in every possible way; and, lastly, even its easy fusibility, which permits the edges of two sheets to be so completely united by melting together with a strip of lead, that they form a whole for all practical purposes, so that it is possible to make vessels of indefinitely large size and any shape, provided care be taken to support the walls of the vessel on the outside, lest they collapse by their own weight.

A special advantage of lead is this, that even after a number of years, when the chambers have become quite worn out, the greater portion of its value can be recovered by remelting the material; even the mud containing lead can be utilized.

The attempts to make sulphuric-acid chambers from other materials than lead have completely failed. To this class belongs the proposal of Leyland and Deacon (patents of September 10th and December 2nd, 1853) to make them of hard-burnt firebricks, slate, sandstone, basalt, &c., set with a mixture of melted sulphur and sand. *Vulcanized india-rubber* or *gutta percha* are just as useless; Krafft (Wagner's 'Jahresb.' 1859, p. 137) found that gutta percha in an acid-chamber loses six times as much weight as lead, and half as much again of its surface. It would be absolutely impossible to use it, because it softens at the temperature of the chambers, and in that state is even more easily acted upon by the gases. Simon's *zeiodelite* (Dingler's 'Journal,' clv. p. 100), a mixture of 19 sulphur with 42 pounded glass, to be employed in slabs of ½ inch thickness, has, no doubt, never been so much as tried for this purpose, no more than the *sheets of glass* proposed by Wilson and others.

We will now describe the *erection of lead chambers.*

The chambers are always placed at some elevation above the ground-level. At the present day chambers are probably nowhere found placed on the ground itself, or on such low foundations that one cannot at least walk underneath; mostly their bottoms are much higher than this. The first object of this is to give the opportunity of ascertaining whether the chambers are tight. If their bottoms are not easily accessible, large quantities of sulphuric acid may get lost in the ground before any loss is detected. And this means not merely a loss of the acid, but still more: the foundations get corroded and undermined, and the whole structure may collapse. The expense of building the chambers on pillars &c. is not thrown away, as the whole space underneath can be used as a warehouse which in winter time has always a moderately high temperature; or it may even, if high enough, be utilized for the pyrites-kilns &c., although this course is not to be recommended. In the latter case it should be from 17 to 20 feet high. At some works, which are pressed for space, even the saltcake-furnaces, ball-furnaces, &c. are built underneath the chambers; but the space below them must then be at least 30 feet high.

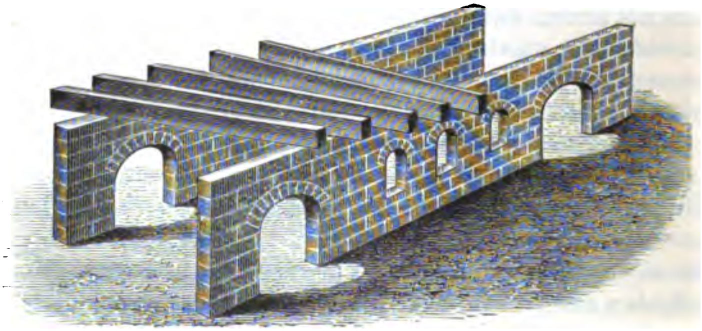
In any case the soil must first be examined to ascertain whether it affords a safe *foundation*; for if it settles more in one place than in another, the chamber gets out of plumb and its bottom out of level, which, owing to the acid lying on the latter and to the instability of the chamber-sides, causes great inconvenience. A rocky or pebbly ground is best; next to this, sand or clay; marl or limestone are bad, because sometimes acid will run over accidentally, which acts upon it; and this may happen even with clayey soil. In such cases the whole soil underneath the chambers must be protected by a layer of asphalt.

The pillars upon which the chamber is erected must, of course, go down to the "rock," as in any ordinary higher building. If the accumulation of made ground or loose earth is so deep that it would be too costly to excavate and raise the pillars from below, piles must be driven in, according to well-known building-rules, and the pillars built upon these.

The pillars themselves can be made of brickwork, stone, cast-iron, or wood. Sometimes, instead of single pillars, two longitudinal walls are erected, connected by cross joists and interrupted by doors, windows, &c., as shown in the sketch, fig. 139. Such long walls take much material and make the room underneath the chambers dark, in spite of the windows. They are only suitable where the chambers are placed unusually high in order to build furnaces underneath. Up to a height of about 26 feet metal pillars seem preferable.

The cheapest pillars are those made of wood or bricks; very rarely they are made of stone—much more frequently of the dearer but much stronger and more durable material, cast-iron. If made of wood, round or canted balks of at least 10 inches (better 12 inches) thickness must be employed. Mostly fir- or pine-wood is used, especially Scotch fir; but the American pitch-pine or yellow pine, such as is used for ship-building, is preferable (on account of its much greater durability) in spite of its higher price. This applies not merely to the foundation pillars, but even more to the frame of the chamber itself. The pillars must vary in their thickness, mutual distance, and manner of being stayed, according to their height and the weight resting upon them (which may be taken at 150 lbs. per superficial foot of the total chamber-area, for the lead, timber, and acid, the latter alone in a full chamber amounting to 120 lbs. per superficial foot); but for an average height of 10 to 13 feet, which will not often be exceeded with wooden pillars, they ought not to be further apart than 10 to at most 13 feet from centre to centre. In any case they are put into a stone socket projecting from the ground, lest the bottom of the pillar be damaged by any moisture or acid; the stone has at the top a hollow of ½ to 1 inch depth, into which the foot of the pillar fits exactly; at first a little tar is poured into it. Wooden pillars do not last for ever; they are not to be trusted very much, and are rarely found now in larger works, at any rate as principal pillars, except where wood is very cheap.

Fig. 139.



Frequently *brick pillars* are employed. These also are not often made above 13 feet, at most 15 feet high; they are at least 18 inches (better 2 feet) square. They are made of common bricks with a mortar very poor in lime.

The brick pillars in many works have been replaced by cast-iron ones, because they are not very durable, especially at the top, where the beams rest. Even the bricks themselves become rotten by contact with the acid, and only stand better if previously soaked in hot tar; but they take the mortar very badly after that. They may also be painted with hot tar afterwards.

On the Continent, where, in consequence of the colder winters and hotter summers, the chambers have to be placed in a closed building, the pillars may be built in a piece with the main walls of this building; but it is even then best to keep them separate, as their settlement is different from that of the main walls.

Chambers 20 feet and upwards in width are sometimes built with mixed pillars—viz. brick pillars for the two long sides, and wooden pillars for the centre row.

Stone pillars are not often used for acid-chambers. Made of rough stones, they would be extremely clumsy; and hewn stone in most places is too dear. On the other hand, of course, stone pillars of the latter kind are very substantial, and last almost for ever, unless the stone be very soft and rotten.

In the larger works in England *cast-iron* pillars are almost exclusively employed, in spite of their higher cost. These can be made 30 or even 36 feet high; they take very little space, and are almost imperishable if painted from time to time. They can be

Fig. 140.

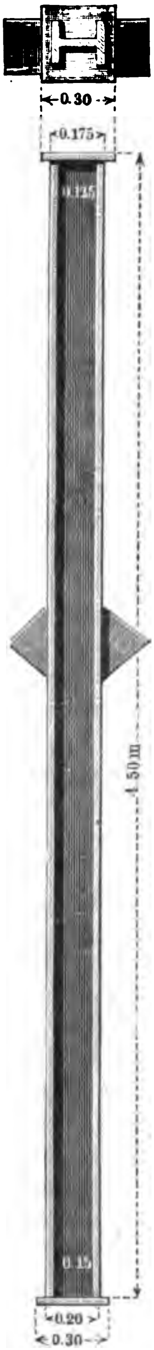
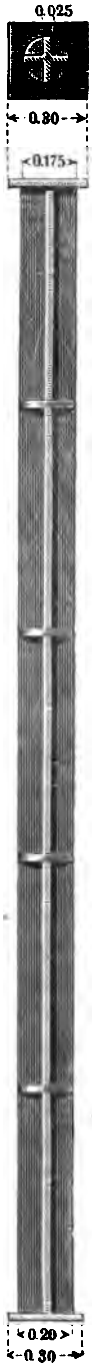


Fig. 141.



$\frac{1}{30}$

weighted a good deal more than any other pillars, unless these are made very thick; and they can be used as supports for many other purposes by means of cast-on brackets or even of pieces bolted on subsequently. A brick or stone foundation must be made for them up to the level of the ground or a little higher; the top stone is made with a socket to receive the foot of the pillar, as in the case of wooden ones; or holes are drilled into the stone, corresponding to other holes in the base of the column; and the joint is made by iron cramps, fastened by pouring in melted lead, or in some other way.

The cast metal columns are now frequently made of an **H**-shaped section and a little tapering upwards. Fig. 140 will show this more distinctly together with a bracket on each side for receiving a wooden stay for the timber above. Another, cross-shaped section is shown in fig. 141. These constructions are better adapted for brackets, &c. than round columns. If higher than shown in the figures (15 feet), they must be correspondingly stronger—for instance, for 20 or 24 feet height, 12 inches diameter at the base. Such columns can be placed at 20 feet distance from centre to centre, if the beams resting upon them are strong enough.

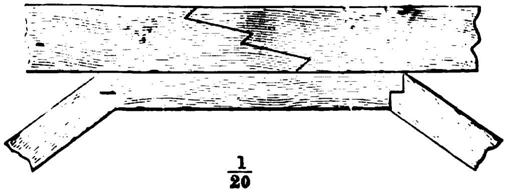
Sometimes the columns are made of wrought iron, of the section shown in fig. 142. They are a little dearer than cast-iron columns, but more durable and reliable.

Fig. 142.

The pillars are in most works placed so that they stand directly under the side frame, which has to carry the weight of the chamber sides, and in the English system also the whole weight of the chamber top. This, however, in any case suffices only for very narrow chambers; for chambers of ordinary width (from 20 feet upwards) a centre row of pillars must be added to prevent sagging of the joints. But as the weight of the acid in a full chamber may be up to four times as much as that of the frame and lead combined, it seems more rational to place the pillars more inside, in which case two rows suffice even for a chamber of ordinary width.

Above the pillars there are generally, in England, *longitudinal sleepers.* If there is a continuous wall in the place of pillars, to cover this with a 2-inch plank will be sufficient; but if there are separate pillars, the sleepers must be strong enough to support the whole structure of the chambers, both wood and lead; and their strength will then depend on the distance between the pillars. With chambers of 20 feet height, and distances between the pillars of 20 feet from centre to centre, the longitudinal sleepers should not be less than 12 to 14 inches high, and ought, besides, to be supported by stays, as shown in fig. 143. With the pillars at shorter distances (say 10 or 13 feet), timber of 9 by 12 inches, always on edge, suffices for the longitudinal sleepers. The joints of the beams of which they consist ought to be well connected, as shown in fig. 143, and should be placed between the pillars, where they are supported from below by the stays. The upper face of the sleepers must be levelled as well as possible from one end of the chambers to the other. Above these the *cross joists* are placed, running from side to side, and made long enough to carry the side frames, and to leave, moreover, a passage round the chambers. For the latter object only every third or fourth joist need project about 5 feet on each side. The joists are mostly planks on edge.

Fig. 143.



$\frac{1}{20}$

If chambers are much less than 20 feet wide, which rarely happens now, no centre longitudinal sleeper is needed, and the cross joists should have 9 by 3 inches section and corresponding length. Wider chambers require a centre row of pillars and sleepers; and in this case, as such long planks are not easy to get, the joists can be made in two lengths, resting on a side and on the centre sleeper. The horizontal distance of the floor-joists is usually 12 inches from centre to centre. Some works have them 3 by 11 inches. The length of the joists is equal to the width of the chambers *plus* the chamber-frame, *plus* the width of the passage.

The joists are covered with a 1-inch *floor*, laid quite level in all directions. As the flooring-boards might easily warp afterwards from the heat of the chambers, this must be prevented by the well-known methods of carpentry. The edges of the boards are planed so as to form a perfectly smooth floor without any chinks.

Another system of building is more in favour on the Continent. First, from pillar to pillar strong sleepers are laid across the width of the chamber; upon these a large number of longitudinal joists are laid, and the flooring-boards on the top of these, running from one side of the chamber to the other.

Upon the whole the *frame of the chamber* is erected, which serves for supporting the lead. It consists, for each side of the chamber, of a sole-tree (sill) and a crown-tree (capping), connected by uprights or "standards," and further tied by cross rails or stays. The sole- and crown-trees and uprights are either of square section (say 6 inches square for a chamber up to 20 feet high) or oblong (say 7 by 3 inches). The sole- and crown-trees lie on the flat side; and the uprights are mortised into them so that their longer side just covers the trees. In the corners the trees project over and are rabbeted into each other. If no cross rails are employed, the uprights are placed 3 feet 3 inches apart from each other; if they are connected by cross rails, they can be placed 4 feet apart. The cross rails are 3 inches by 2 inches; they are only partly let into the uprights, in order not to weaken these; and are placed at vertical distances of 4 to 5 feet from each other. The chamber-lead is kept a little away from the woodwork in order to expose the lead always to the cooling action of the air. If this is not done, the lead is found to be quickly corroded in the parts protected against radiation of heat by the wood; it has even been observed that insects from the wood have bored through it *. It is becoming more and more the fashion to shape the woodwork so as to present the least possible contact with the lead, as shown in figs. 144 and 145. Almost the same effect is obtained by using round timber for uprights.

Fig. 144.

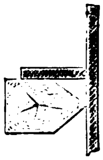
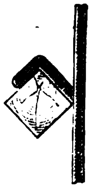


Fig. 145.



The best kind of timber for this purpose, as well as for all others

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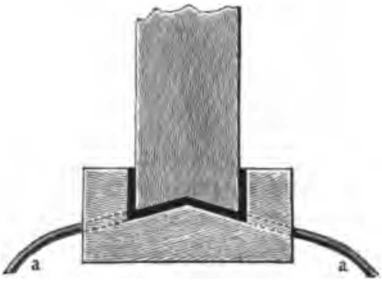
* I have described such a case, where the beetles in question belonged to the species *Tetropium luridum* and *Hylotrupes bajulus* (Zsch. ang. Chem. 1897, p. 527).

where acids are concerned, is American yellow-pine or pitch-pine; but as this is frequently too expensive, ordinary red-wood is also very much in use. It is beneficial to protect it against the action of the acids by a coating of whitewash, which is at the same time a slight protection against the risk of fire. Another kind of protection from the former, although not from the latter, risk consists in painting the woodwork with coal-tar, or preferably with a sort of tar-varnish, made by dissolving coal-tar pitch in heavy tar-oils, and known as "prepared" or "refined" tar (Lunge's 'Coal-Tar and Ammonia,' 3rd edition, p. 374). The latter enters better into all the pores of the wood and on drying does not leave so many crevices; it is altogether preferable to raw coal-tar for painting wood, iron, or brickwork, and is not much dearer.

The painting of the woodwork is best done twice, and before the lead is put on, so that all parts can be reached by the brush.

Special care must be taken lest any acid gets into the mortise-holes, where the uprights are joined to the sole-trees, &c. No empty space should be left here where any acid could lodge, but all interstices should be filled up with coal-tar pitch or the like. It seems also another good plan to cut out the bottom of the upright, and make it fit on to a corresponding saddle-shaped part of the sole-tree, as shown in fig. 146. Two small lead pipes drain away any liquid collecting in the low corners, so that no acid can ever lodge there and cause the wood to decay.

Fig. 146.



In France sometimes the bottoms of the uprights are not at all mortised into the sole-tree, but rest flatly upon them, being kept in their places by pressure and friction only.

Whether cross rails are used or not, in any case there should be diagonal stays, to give more stability to the frame. It is not of much consequence how the stays are put, so long as this is done according to the well-known rules of carpentry.

If, as is usual in England, the chambers are in the open air, one side of the frame is made about a foot higher than the other, so that the rain-water and melted snow can run off, and on the lower side a water-spout is arranged so that the rain-water cannot run along the chamber-side down into the acid at the bottom.

At some places the chamber-frames are made of *angle-iron.* This plan has the advantage of presenting an extremely durable and clean erection and of avoiding overheating of the lead in any part. Such frames may be constructed in the following manner. The side-frames consist of thin angle-irons crossing each other at right angles, the uprights 9 ft. 6 in. and the horizontals 7 feet distant from each other. No iron nails are employed at all; the lead straps are simply bent round the angle-irons. The roof is suspended from angle-irons in exactly the same way. Of course iron frames are more costly than wooden and must be kept in order by painting from time to time, preferably with coal-tar varnish (p. 429).

Now the *chamber* itself can be erected, and we shall therefore now speak of the *lead* to be employed. For this, sheet-lead as wide as the rolling-mills can supply it, and of convenient length, is used, so as to have as few seams as possible. The usual thickness in England is 6 lbs. to the superficial foot, sometimes 7 lbs., especially for the ends and the top, or for the first chamber of a set.

This thickness is sufficient for a chamber to last upwards of ten years; the bottom lasts longest, because it does not get so hot as the sides and the top, and it is also more protected by the mud of lead sulphate which collects upon it; only in cases of gross neglect (for instance, if nitric acid gets to it) it is quickly worn out, whether the lead be thick or thin. But where *zinc-blende* is used, the *mercury* contained in it may have a different effect, especially since the blende-furnaces are driven at a higher temperature, so that more mercury gets into the chambers. According to information received from Dr. Hasenclever in 1902, it has been noticed at Stolberg that the mercury acts most strongly at the lateral parts of the bottom which are less protected by the sulphate-of-lead mud, and where the joint between the side sheet and the bottom sheet causes the double layer of lead to collect acid and mercury between the two sheets. Here sometimes mercury is visible in globules, and that part is worn out in less than three years. Hence they make the whole bottom of stronger lead, rolled extra strong at the part next to the sides, which is, moreover, protected by a covering of acid-proof flags.

In America the usual thickness of lead is only 5 lbs. per superficial foot, and even 4 lbs. lead is sometimes used (Journ. Soc. Chem. Ind. 1885, p. 27); but this seems very bad economy indeed, and it can only be done when burning brimstone. In the best American works I have found 6 lbs. lead.

On the other hand, at some of the best English works not only is 7 lbs. lead used throughout for the chambers, but in the most exposed places, such as the front and back ends of the leading chamber and several feet of the sides adjoining these, 9 lbs. is used. Sometimes the side sheets are rolled so that the upper and lower two feet are made stronger than the remainder, because these parts are more quickly worn out. Chambers built in this careful way last upwards of 20 years.

The *quality* of the lead is certainly not indifferent. Opinions were formerly not altogether agreed as to the point whether pure or impure lead better resists the action of sulphuric acid; and in the present case it is no doubt not so much this acid as the nitrous compounds to which the attack of the lead is due. Most manufacturers formerly inclined to the belief that "hard" lead is better adapted to vitriol-chambers than "soft lead." A test sometimes performed consists in trying which of several samples of lead in contact with sulphuric acid gives off more hydrogen from a given surface in a given time; but this test is very apt to mislead, and there is really no good test known as yet (comp. Journ. Soc. Chem. Ind. 1884, p. 230).

This subject has been fully discussed before, p. 206 *et seq.*, where the conclusion was come to that for vitriol-chambers the *purest* and *softest* lead is the most suitable material. In Zsch. ang. Ch. 1892, p. 643, I have given the following analyses of lead specially suited for vitriol-chambers:—1. Soft lead of the Mulden lead-works: 0·001 per cent. Cu, 0·044 Bi, 0·0004 Sb, 0·0005 Fe, 0·0004 Sn, 0·0005 Ag, no As. 2. Soft lead from W. Leyendecker & Co., Cologne: 0·0034 Cu, 0·0019 Bi, 0·0029 Sb, trace of Fe, 0·0047 As, 0·00025 Cd, trace of Ni & Co, 0 0010 Ag, 0·0002 Zn, 0·0024 O.

G. E. Davis ('Chemical Engineering,' i. p. 142) quotes the following analyses of "chemical lead" (from what source or by whom made is not stated); the figures indicate milligrams per kilogram (I omit the decimals):—

	A.	B.	C.	D.
Antimony	17	19	64	32
Copper	21	13	14	19
Silver	22	14	39	16
Iron	3	2	12	2
Cadmium	1	1	1	2
Bismuth	4	2	22	4
Zinc	2	1	2	3
Sulphur	1	2	2	1

According to Eng. & Min. Journal, March 8, 1902 (Journ. Soc. Chem. Ind. 1902, p. 510), a special brand of lead is designated in Missouri "chemical hard lead" and is sold at 5 cents per 100 lbs. above the price of common Missouri lead. It is supposed to contain a little copper and antimony, but no attempt is made to keep the composition within precise limits. Mühlhäuser, in Zsch. angew. Ch. 1902, p. 758, quotes an analyses of soft chamber-lead from Chicago and St. Louis.

Leyendecker (B. P. 2756, 1901) prepares a special quality of chemical lead by adding either 0·1–0·5 per cent. copper or 0·1–0·5 per cent. copper and 0·1–0·3 per cent. antimony. (Such a patent could hardly be maintained in the face of my researches, p. 206 *et seq.*, published a long time ago, for the purpose of benefitting chemical manufacturers generally.)

The analysis of such lead, which I have obtained from the Rhenania Chemical Company, as compared with ordinary soft lead, gives the following results :—

	Ordinary soft lead.	Leyendecker's special quality.
Bi per cent.	0·00501	0·00605
Cu „	0·01787	0·06683
Cd „	0·00004	0·00003
As „	0	0·00002
Sb „	0·00039	0·05025
Fe „	0·00089	0·00074
Zn „	0·00082	0·00122

We notice, in the "special quality," besides a certain amount of copper and antimony (the latter in such small quantities as not to counterbalance the useful effect of the copper) also an extraordinary small amount of bismuth, being only 1/100 of that present in the "ordinary soft lead." The firm using both had not had a sufficiently long experience with them to judge of any difference in behaviour.

Another "special quality," particularly recommended for Krell's concentrating apparatus (comp. Chapt. IX.), is supplied by Graffweg & Co., Düsseldorf. It is probably something very similar to Leyendecker's lead.

All sheet-lead before being used should be "mangled," in order to beat out all inequalities and indentations casually produced in transit &c. For this purpose it is tightly rolled round a wooden roller, about 6 inches thick, and is beaten all the time with a plumber's mallet.

The sheets of lead were, in the infancy of acid-making, joined together by the ordinary *soft solder*, which is very convenient for use, but is soon corroded by the acid. Places soldered thus are also much more brittle than pure lead. So long as the chambers had to be put together in this way, there was occasion for innumerable repairs.

Another plan (which is far better in this respect, but takes much lead, and is only easily applicable for straight seams) is the *rabbet*-joint. The edges of two sheets of lead are turned over in the way shown in fig. 147, placed one into the other, and beaten down on a smooth surface. Such joints are gas-tight, and have been used here and there in England till within the last few years.

Fig. 147.

The kind of joint now generally employed is that made by *burning*, with the lead itself—that is, by melting it with a hydrogen flame fed by compressed air. In this way the two sheets are joined so tightly, that with good work the joint, being thicker than the sheets, is actually stronger than they are. If the work is rough and uneven, foreign substances will easily be deposited in the rough parts, by which the lead may be damaged.

This mode of joining was invented by Debassayns de Richemond in 1838. Two apparatus are required for this, whose construction is seen in figs. 148 & 149. Fig. 148 shows the "plumbers' machine" —that is, the hydrogen apparatus—quite similar to an ordinary laboratory gas-holder, but made of lead, often with a wood casing. The lower vessel, A, contains a lead grating, KL, upon which granulated or scrap zinc is put. The upper vessel contains dilute sulphuric acid. The connecting-tube with a cock *f* allows the gas to pass out of the opening C, after it has first been washed in a water-vessel. Often there is a plain outlet just above the cock *f*. The outlet is connected with a long india-rubber tube, by means of which the gas can be conducted to a distance. The tube G serves for running sulphuric acid from B to A. It can only run in as gas is allowed to escape by opening the cock *f*; and thus a continuous current of gas is obtained. The openings D, E, and F serve for introducing acid and zinc, and for running off the solution of zinc sulphate.

Fig. 148.

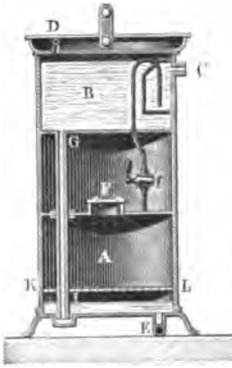
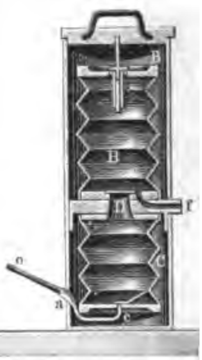
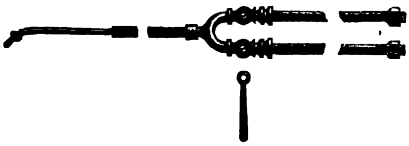


Fig. 149.



The second part of the apparatus, which is shown in fig. 149, is simply a portable smith's-bellows of cylindrical shape, the lever of which, *o a c*, a boy works with his foot. The air is forced through the valve D from C to the closed air-vessel B, and escapes through the opening *f*, likewise connected with a long elastic tube. The two tubes are united by a blow-pipe, fig. 150; and the mixture is ignited. Each limb of the blow-pipe is provided with a stop-cock, by turning which the plumber may admit more air or hydrogen

Fig. 150.



at will, and thus can produce a flame of any size, which, however, should never be an oxidizing one.

The mouth-piece of the blow-pipe itself is sometimes connected with the fork-shaped piece by a short elastic tube, to make it more mobile. Besides the ordinary mouth-piece, ending in an aperture of about $\frac{1}{25}$ of an inch diameter, the plumber also carries another, provided with a small brass shield, to obtain a steady flame in windy weather. The gases unite only immediately before escaping; and thus the flame cannot strike back. By means of this machine a pointed and very hot hydrogen flame is produced, which, at the place where it touches, melts the lead immediately down to a certain depth ; and the art of burning consists in touching and melting parts of two sheets *at the same time*, which, on cooling, solidify to a whole.

It has happened that plumbers have been poisoned by arseniuretted hydrogen, produced by impurities in either the zinc or the sulphuric acid. The hydrogen can be freed from this by washing it with a solution of cupric sulphate, by which the arsenic is precipitated. Hydrochloric acid should not be employed for evolving the hydrogen, even when free from arsenic, as the workmen are injured by gas thus made.

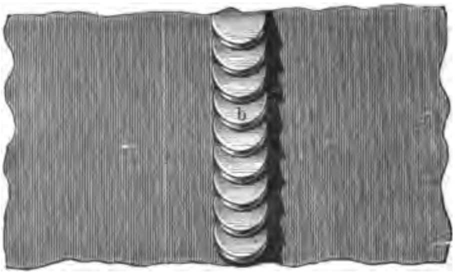
The *burning* itself is a kind of work requiring much practice, because the plumber must not allow the flame to act a moment too short or too long. If he does the former, the fusion is not perfect and the seam is not tight; if the latter, he burns a hole in the lead. Wherever it is possible, one sheet is laid about 2 inches over the edge of the other, as shown in fig. 151. The seam is made with the help of a strip of lead, about $\frac{5}{8}$ by $\frac{1}{4}$ inch thick, which the plumber holds in one hand whilst he guides the blow-pipe with the other. He works in this way :—He touches with the flame the place *a* (fig. 151), where the edge of one sheet lies upon the other, so that the surface of the lead (previously scraped clean) just melts, but the back part of the lead does not melt. At the same time he holds the above-mentioned strip in the flame, so that drops fall from it on to the just-melted part

Fig. 151.

of the sheets, and the whole is united into a seam, *b*, all fusing together into one mass. By a slight motion of the wrist the plumber removes the flame for a moment, and the lead, which has only just been melted, at once solidifies; in another second the flame is again directed upon the lead, and a new drop flows partly over the first one; so that at last the whole seam takes the shape shown in fig. 152.

Although all this is much more easily described than carried out successfully, still the burning of *horizontal* seams is learned in a comparatively short time, and can be done very quickly by a practised workman. In windy weather it is certainly much more difficult, and in rainy weather it is not possible at all.

Fig. 152.



The burning of *perpendicular* (upright) joints is much more difficult, and, even in the hands of the most experienced workmen, takes at least three times as long for the same length of seam as horizontal burning, without ever being as strong as the latter. This is easily understood; for the melted lead, which quietly remains lying on a horizontal sheet, in upright burning at once runs down; and this can only be prevented in one way: the lead must be heated exactly up to the melting-point, and the flame instantly removed till the seam has solidified; and the burning must always be done from the bottom upwards, so that to a certain extent the seam will retain the drops of lead. In this case not much use can be made of strips of lead for strengthening the seam.

A practised plumber can burn as much as 10 feet upright or 25 feet horizontal joints in an hour; but such figures are only reached in piece-work.

Recently the burning of lead has frequently been effected by a pure *oxyhydrogen flame,* both oxygen and hydrogen being applied in the compressed state, contained in steel cylinders. The burning in this way is done much more rapidly. Suitable burners are sold by the Sauerstoff Fabrik, Berlin, O.

Water-gas can be employed for lead-soldering without a blast of air (or oxygen), but its poisonous properties must not be forgotten.

The way of erecting a lead chamber in England is usually as follows :—The commencement is made with the sides, for which the sheets are made as wide as possible (most lead-rolling mills supply them up to 7 feet 9 inches, some even wider), and so long that they extend 4 inches beyond the height of the chamber, of course taking into account that one side of the chamber is a foot higher than the other. 6 inches are reckoned to turn over the crown-tree; but 2 inches are saved at the bottom, because the lead afterwards expands by the heat of the chamber.

Now, on the wooden floor before mentioned a wooden table (the "sheet-board") is constructed, held together at the back by battens, but quite smooth on the upper surface. It has the width of two or three sheets of lead (that is, 15 feet 6 inches, or 23 feet 3 inches) and the height of the chamber—which, of course, can only be done when (as is generally the case) the chamber is at least as wide as it is high. On this table the sheets of lead are rolled out flat, placed side by side, so that one overlaps the other 2 inches, and burned together; at the same time all the straps (of which we shall speak directly) are burnt to the lead, which can be done because the upper surface will afterwards be the outer one. The upper edge is bent round the sheet-board, so as to hold it fast; and when everything is finished this end is wound up by a set of pulleys, so that the sheet-board is raised along with the sheets of lead, and lies flat against one side of the chamber-frame. Now the upper edge of the lead is at once bent over the crown-tree and nailed down, as well as all the straps. For this no cut or wire nails are ever used, but wrought nails with broad heads ("plate-nails"), about 1½ inch long, whose heads are all protected against the acid by dipping a few at a time into melted lead. When the lead has been completely fastened to the frame, the sheet-board is lowered down, moved forward its own width, and another piece of the chamber-side made upon it, till in this way the chamber-sides and ends have been finished all round. Only in the corners it is preferable to use single sheets, which form a rounded corner: this is much stronger than a sharp edge. The object of the described process is this, to reduce the upright burning to a minimum. It is much better than the former plan of hoisting up each single sheet, turning its margin over the crown-tree, and unrolling the sheet by its own weight. In this case every single sheet had to be joined to its neighbour by upright burning, and the straps had to be burnt on in an equally inconvenient manner. If at all possible, the seams ought not to be behind the uprights, so as to be better accessible for repairs; and for this reason also it is to be recommended to make the chamber-frame as shown in figs. 144, 145, or 153, where the uprights do not touch the lead at all.

The *straps of the sides* must be arranged according to the style of the frame. If this only consists of uprights mortised into the crown- and sole-trees, without any cross rails, the straps consist of perpendicular pieces of lead nailed sideways to the uprights with five leaded nails each. The strap ought to be long enough to turn over the edge of the upright, so that two of the nails come to the front (fig. 155, upper part). Such straps are placed alternately on one and on the other side of the upright, one about every 4 feet. These straps do not allow the chamber-lead to follow the changes of temperature by extension or contraction. This easily leads to deformation of the sides and tearing off of the straps; and it is therefore better to avoid this, which can only be done by nailing down the top strap in this way. For the lower straps longer pieces of lead are burnt to each side of the upright, which meet on its front, and are there joined by rabbeting (see fig. 155, lower part, and fig. 156). There are no nails used here; so that the lead walls may move up and down the upright, whilst at the same time they are all the more stiffened by being held fast in two places. This, of course, takes more lead and labour than simple straps. In each case the straps are about 8 inches in depth.

The object of keeping the lead clear of the wood, and of giving it scope for expanding, is well attained in the form of strap shown in figs. 153 and 154. The upright *a* is placed with one of its edges pointing towards the chamber. The strap *b* turns round the edge of *a*, and is fastened to it, not by ordinary nails, but by a broad-headed pin *c*, which passes through a slit 2 inches in height. This arrangement allows the strap to work up and down, as the chamber-side expands and contracts.

Fig. 153.

Fig. 154.

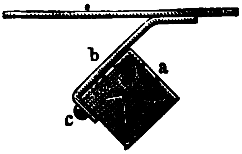


Fig. 155.

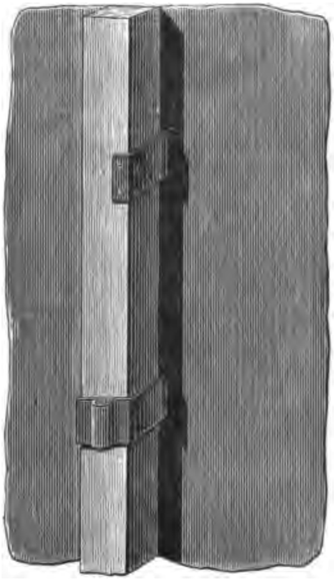
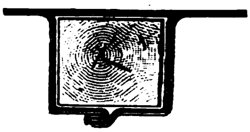


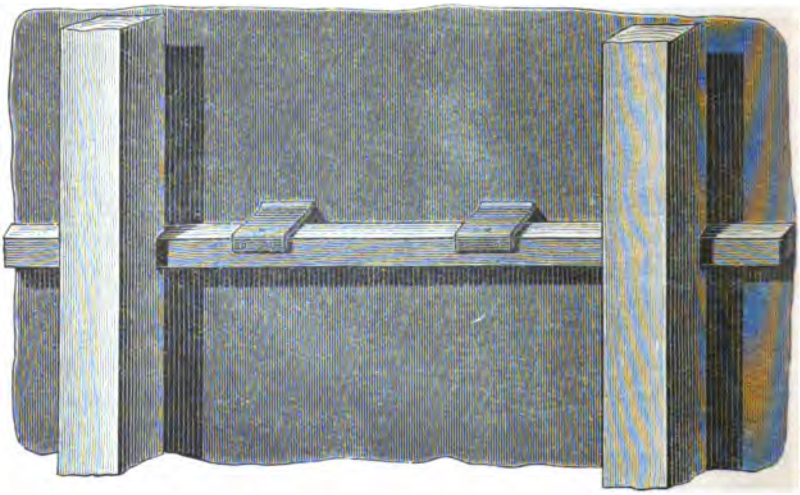
Fig. 156.



If the frame is provided with horizontal cross rails, only a few upright straps are used—sometimes none, only horizontal ones, turned down over the rail, and nailed to it (fig. 157), two of 6 inches length for each rail. This kind of straps protects the chamber-sides much better against deformation than the upright straps, and carries the weight better upon the frame (this is confirmed by information from Stolberg in 1902) ; it also permits the lead to be kept further apart from the wood, since the straps may leave about ½ inch (not more) space between the lead and the rails. The diagram shows this.

The chamber-sides can also (as at the Thann Works) be made of horizontally disposed sheets of lead. The overlap in this case is nailed to the horizontal cross rails in lieu of straps, as shown in fig. 158; but first the whole height of the chamber-side is finished, the whole is rolled upon a wooden roller, and allowed to unwind itself by its own weight from the top. In this way there is not so much pull upon the seams as if the chamber were made of sheets hanging down by their length, since each sheet is supported just in the place where there would be a pull. This plan, indeed, seems

Fig. 157.



to be worthy of general recommendation; for it saves the lead and labour of all the straps, and supports the chamber very well.

At least as substantial is the plan used at Aussig. There are no side-straps at all; but to each upright of the frame corresponds a strip of lead burnt to the chamber-side along its whole height, probably the lap turned outside. This is nailed sideways to the upright. Between this and the lead there is a wooden lath, to increase the contact of air with the chamber-lead as much as possible. Fig. 159 shows this in horizontal section.

Fig. 159.

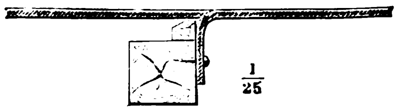
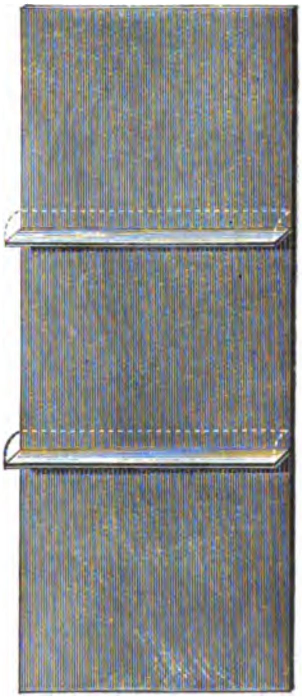


Fig. 158.



Mr. Benker ascribes great advantages to his *perforated straps*, shown in figs. 160 to 162. Fig. 160 is a plan, showing the chamber-side *a*, the uprights *b*, the cross-bars *c*, the small wooden bars *d*, and the straps *e*. The same parts are seen in vertical section in fig. 161. The chamber-lead is kept 2 or 2½ inches apart from the cross-bars; the perforations of the straps (which may extend the whole width of the cross-bars, as in fig. 162) cause a strong current of air to rise upwards and cool the lead, without allowing any quantity of dust to accumulate on the straps. This system is especially good for chambers which are driven hard for "forced work."

In the first-described case, now generally used in England, at first only about a yard of the seams is burned, and that at the top, so that the chamber can be covered in and the remainder can be done at leisure in bad weather. The next thing, therefore, is the *chamber-top*. For this we need a temporary scaffolding, movable

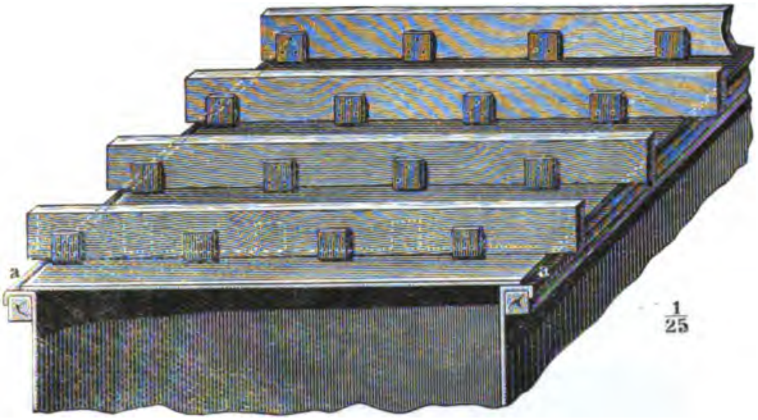
Fig. 160.

Fig. 161.

Fig. 162.

on wooden rollers, made of high trestles joined together at the top, equal in height and width to the chamber, and in length to at least two (or, better, three) sheets of lead. This scaffold is put together within the chamber itself, its separate parts being got in by bending back one of the side sheets. It is covered on the top with a flooring of boards; and upon this the sheets serving for the chamber-top are flattened out. These are a little wider than the chamber, so that they project 3 inches on each side. Thus they do not project quite as far as the overlap of the side sheets (6 inches), and there remains a joint suitable for burning (fig. 163, *a*), which is burned very strongly. Now the sheets

Fig. 163.

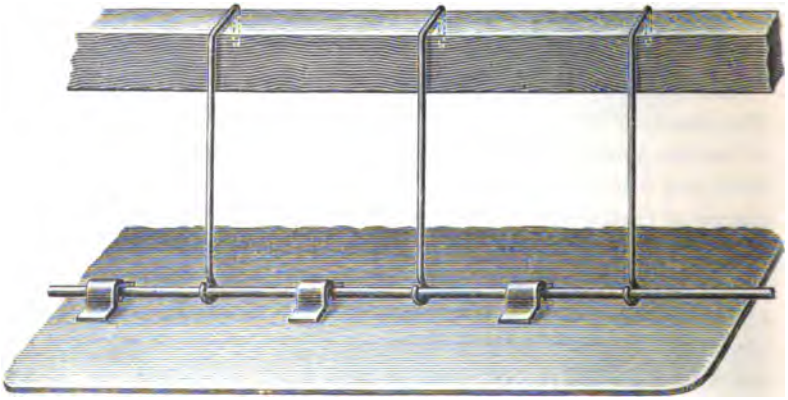


themselves are joined by burning, and all the top straps are burnt on. The latter, in England, serve for fixing the chamber-top from above to the top joists carrying it. The latter, for a chamber 20 to 26 feet wide, are 3 to 4½ inches thick and 10 to 12 inches high, and are placed at distances of 14 to 18 inches from centre to centre. Their length is at least sufficient to reach to the outside of the crown-trees; it is better if they even project a little beyond, to have a good support. The straps themselves are made 7 inches square, and stand alternately on both sides of the top joists, about 3 feet apart on each side. At other works there are fewer but longer straps. They are bent up and nailed to the top joists laid above them on edge, with five leaded nails each. When all this has been done, the top joists, by the help of the straps, carry the lead of the chamber-top, and the joists themselves rest upon the side frames, but separated from them by the overlap of the chamber-sides. The joists should be well clear of the chamber-top (farther than is shown in the figure), so that air can circulate between lead and wood.

The top joists are protected from canting over by a few boards nailed across them, which at the same time serve as a passage on the chamber-top. Where the chambers are roofed in, longitudinal sleepers may be laid on the top, joined to the top joists by iron clamps, and the whole suspended from the timber of the roof which must be made strong enough for this purpose; but some hold that even with roofed-in chambers it is safer to keep the chamber-top independent of any movement of the roof.

Where the chamber is too wide for any single cross joists, two lengths of these must be joined together and trussed, according to the rules of carpentry; in this case trussed girders may run across the width of the chamber, and the proper joists, to which the top lead is fastened by straps, run parallel with the long sides of the chambers; they are either mortised into the girders, or (which is the stronger plan) they rest in cast-iron shoes bolted to the girders. This, however, is only required for chambers standing in the open air; it is not very convenient, as the side frames have to be weighted very much. Such wide chambers, as we shall see below, have not altogether turned out well.

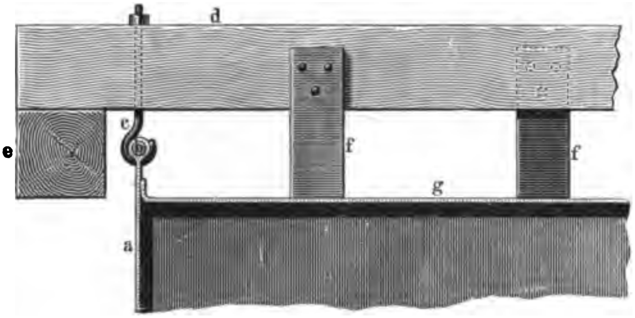
Fig. 164.



Quite different from the just-described chamber-tops are those found in many continental works. There are no wooden top joists, but, in the place of these, thin iron rods about $\frac{1}{2}$ in. thick, fastened to the chamber-top by a lead covering burnt on each side to the chamber-lead. These horizontal rods themselves are suspended from the roofing by means of $\frac{1}{4}$-inch rods placed at short distances from each other. This system cannot be employed for chambers standing in the open air, as it makes the chamber-top dependent upon the beams of the roof; it is shown in fig. 164.

Another system, which may or may not be connected with the roofing, is the following (fig. 165):—The chamber-side *a* is carried somewhat higher up, and bends round an iron rod, *b*, $\frac{7}{8}$ inch thick, the part coming back over the iron being burnt to the other lead. Here and there holes are left for the passage of the iron hooks, *c*, which are bolted to strong joists, *d*. The latter may form part of the roof, or they may be supported quite independently on the crown-tree *e*. The straps *ff* hold up the chamber-top *g*, and prevent it from sagging; the clear space between *g* and *d* is about 8 inches. The object of this arrangement is to prevent all contact between lead and wood even at the top edges of the chambers.

Fig. 165.

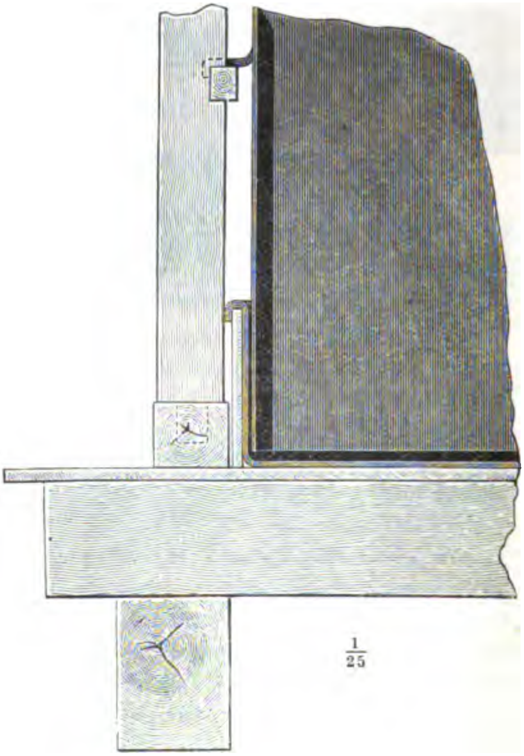


At the Griesheim works, in Germany, the following very rational plan of erecting lead chambers is followed:—On a staging of the whole area of the chamber-bottom, but raised over its top, first the chamber-ends are made; over these, without removing the ends, the chamber-sides are made, first one, then the other, and last of all the sheets composing the top are laid down and burnt together. Thus ultimately five layers of lead are lying on the staging one above another. Then the top straps are burnt on and are joined to the top joists, which are put in their respective places. The whole lead-work is now hung from six differential pulleys, and the staging is removed. As this is done, the ends and sides drop down into their places, and need only be joined in the corners, where they are bent in at an obtuse angle. This mode of procedure causes nearly all the burning to be horizontal, so that the work is done more quickly, cheaply, and substantially.

The *chamber-bottom* is left to the last; and it happens no doubt very rarely (in England probably never) that, according to older prescriptions, the bottom is laid down first and protected by straw and boards while the remainder of the chamber is being made.

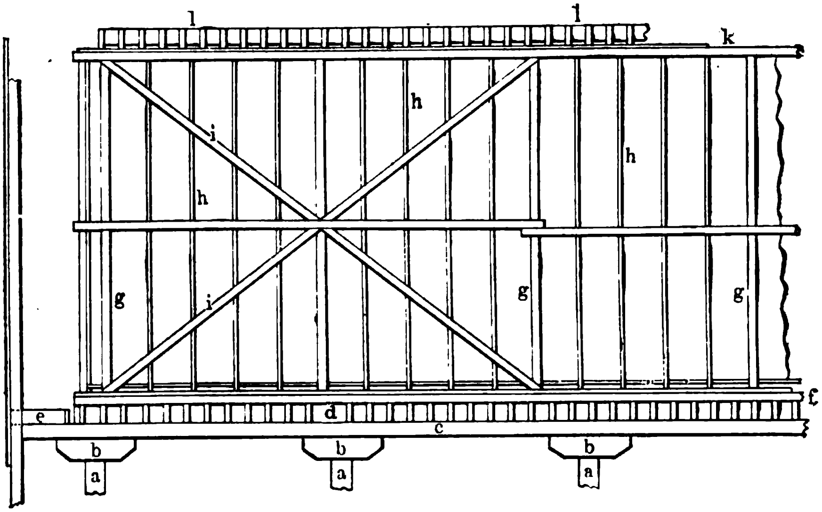
It is, on the contrary, made last of all, but not always in the same way. In some works the side sheets are burned to it all round, and openings are left in a few places for drawing off the acid, for taking samples, &c. In the majority of works the bottom is independent of the sides, and forms an enormous tank with turned-up sides, into which the chamber-sides hang down, dipping into the bottom-acid, and thus forming a hydraulic joint. This allows the chamber-sides to expand and contract with the temperature, and also makes the bottom-acid accessible from all sides, so that it is generally preferred in spite of the larger expenditure of lead; but recently a good many works have adopted the first-mentioned plan of making the chamber as a closed box, which saves both lead and the trouble unavoidably connected with the second system. Often the upstand, or "lag," which should not be less than 14 inches

Fig. 166.



high, so as to afford a good deal of room for acid, is made from a narrow sheet of lead of double width, by bending up one half and leaving the other half to form a portion of the chamber-bottom; the latter is then finished by burning it together with other sheets of lead. This is more convenient for the plumber than taking sheets equal in length to the width of the chamber, along with the height of the upstand on each side. The latter must not be left loose, because it is easily bagged out by the side pressure of the acid; but a 1-inch board is placed all round the chamber-floor, over the edge of which the upstand is turned round and nailed down. This is shown in fig. 166. Instead of a solid board, it is preferable to employ merely a number of perpendicular or horizontal rails, which admit the cooling-action of the air upon the lead. At Stolberg the "lag" is made up to 2 ft. 6 in. high, with a correspondingly strong plank to resist the side pressure of the acid.

Fig. 167.



In some works the bottom is divided into two, three, or four parts by partitions the whole height of the upstand. The object of this is, not to empty the whole chamber in case of repairs; but it is very rarely done, as this arrangement prevents a free circulation of the acid, and as the bottom mostly suffers less than any other part of the chamber—excepting through gross neglect, by the formation of nitric acid, which ought not to happen at all.

Palding (Min. Ind. vii. p. 679 *et seq.*) gives details of chamber construction which refer to the usual English plan, mostly followed in America as well. Fig. 167 shows part of the chamber-side in elevation. The pillars (posts) *a a* are of 14 × 14 inches wood; corbels *b b* 14 × 14 × 5 in.; stringers *c* 14 × 14 in.; joists *d* 3 × 15 in., 16 in. centre to centre, 3 × 2 in. herringbone-strutting; gangway-floor *e* with 2 × 12 in. joists. Of the chamber-frame itself, the sill *f* is 6 × 10 in., with a dowel-pin at each post and toe-nail to each intermediate upright. The strong uprights (posts) *g g* 6 × 6 in., 13 ft. 9 in. from centre to centre; the intermediates *h h* 6 × 2 in., 33 in. centres; the bracing *i i* 6 × 2 in., with lag-screw to each post and spike to each intermediate. Crown-tree *k* 6 × 10 in., with lag-screw at each post and toe-nail to each intermediate upright. Top joists *l l* 3 × 15 in., 14 in. centres, with three lines of solid 2 × 12 in. board-bridging.

Fig. 168 represents a portion of chamber-ceiling, seen from above, and fig. 169 the same in sectional elevation on a larger scale, which clearly shows how the chamber-lead *m* at the top is joined to the sides *n* and turned over the crown *k*, and how the straps *o o* (24 inches centre) suspend the top from joists *l l*. Fig. 170 makes this clearer by a side elevation, and fig. 171 shows the way the straps are cut from a strip of rolled lead.

Fig. 172 gives a plan-section of a chamber-corner, and fig. 173 a sectional elevation of the lower part of a chamber, showing how the straps *r r* are fastened to the uprights *g*, *h*, and how the lead side *m* and the saucer *p* stand off. Lastly, fig. 174 shows how the upstand *p* of the saucer is turned over ledge *s* (2 × 1 in.), and held at the bottom by another strip *t* (3 × 2 in.), spoked to the sill.

In England, where the winters are not severe, lead-chambers are hardly ever roofed in, but are only built so that the rain-water can run off as described above. But even then the space between each two chambers must be covered by a light roof, and the whole set must be surrounded by a wooden shed, because a gale might tear the lead off the frames, or even throw down a chamber altogether. These wooden houses have windows or Venetian blinds, changed according to the wind. In windy places they are always made first, as soon as the foundations and the frame are finished, but before the lead has been fastened to the latter, because during the building the incomplete chamber is even more exposed to being thrown down by a gale than after completion.

Fig. 168.

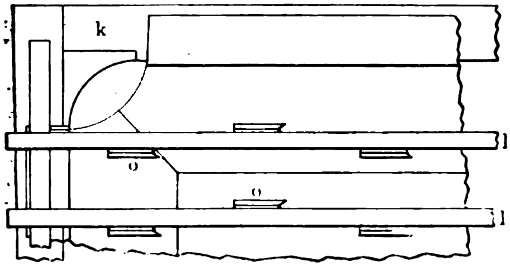
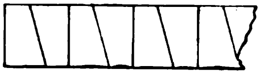


Fig. 171.



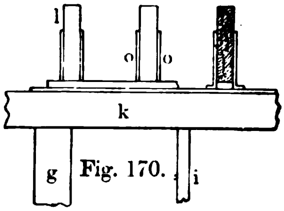


Fig. 170.

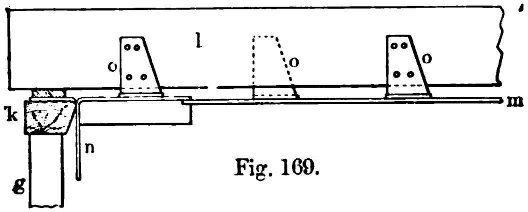


Fig. 169.

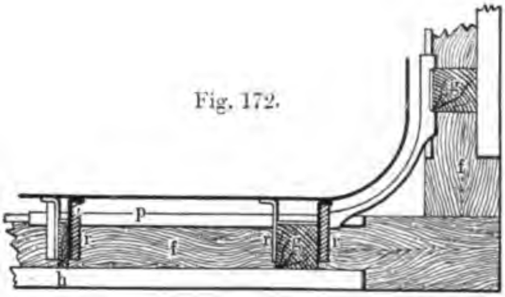


Fig. 172.

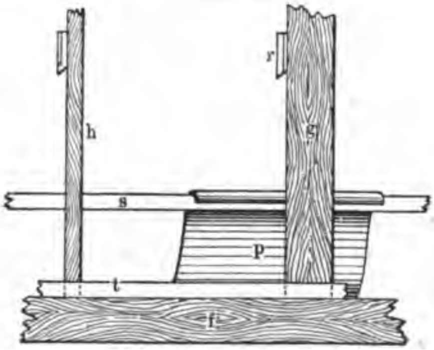


Fig. 174.

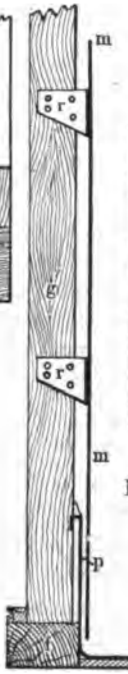


Fig. 173.

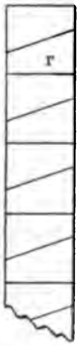


Fig. 175

Thus the chamber-tops are exposed in England to the heat of the sun in summer and to the snow in winter; this is tolerable, because neither of them occurs to an excessive degree. In the less windy places even the chamber-sides are sometimes left without protection against the weather, but never so in well-arranged works. In the south of France, on the other hand, the chamber-tops are always protected against the sun and the rain by a roof; but the sides are generally exposed, which, on account of the heat of the sun there, is certainly very wrong. In the north of France, in Belgium, and in Germany the chambers are always completely enclosed in buildings, usually of a very light construction, and it must be said that this would be decidedly preferable also in the English climate.

Niedenführ recommends placing the chambers on brick pillars, and filling up the spaces between these on the outside with a light wall. The chamber-sides are surrounded by a wooden shed and a light roof, employing roofing-felt as a cover for this. He reckons a square foot of such a building, including the chamber-frame, to cost from 3*s.* to 4*s.* 6*d.*

Renewal of the Chambers.—The greatest wear and tear is experienced in the first chamber, more especially at the front end, and, as some assert, even more so at the back end and the immediately adjoining parts of the sides. Hence the first (leading) chamber is often made of stronger lead than the others. Besides, it must be noticed that any angular parts of a chamber wear out more quickly than round or straight portions. The upright corners are therefore always broken or rounded off; but this is not easily managed with the horizontal top corner. Hence, at some works they make the lead stronger in that place (p. 431). The plan of making the roof partly slanting (p. 454) may do some good in this respect as well, as this avoids a sharp corner. The "curtain," or part dipping in the acid, and alternately subjected to this and to the action of the air, is also liable to quicker wear. There is general agreement on the point that any part of a chamber which gets hotter than the remainder will wear out much more quickly; and this should be guarded against in the construction of the chamber-frame (*suprà*, pp. 438, 441, & 453).

We have constantly laid stress on the fact that the lead should be clear of the woodwork at all points, both because it is thus longer preserved by the cooling-action of the air, and because it is accessible to the plumber. But this condition can, of course, be realized only for the sides and top, not for the bottom. Fortunately the latter suffers least, being protected by the acid itself and by a layer of sulphate of lead. If, however, a leak occurs here after all, it is very awkward to repair. Sometimes this can be done by measuring its distance from the sides, cutting a hole in the chamber-top and dropping down a bucketful of plaster of Paris or, preferably, of a mixture of fresh and burnt pyrites-dust, which quickly hardens into a cake and may stop the leak for years. But if this does not succeed, there is nothing left but to stop and empty the chamber, and to enter through the manhole in order to get at the bottom.

A chamber will last very much longer if the frame be substantially made, and the straps be well burnt on and nailed down and numerous enough, so that they will not be readily torn off. Should this happen, the mischief must be repaired at once: nowhere does the saying come more true "that a stitch in time saves nine." If the repair is put off too long, the chamber-lead, pulled by its own weight, wrinkles irregularly, and the chamber becomes unfit for work much too soon. Especially those parts of the frame most exposed to the action of the acid must be carefully looked after, and, in case of need, at once repaired, before the parts of the lead sides dependent upon them have lost their support and have collapsed. This is most necessary at the junctions of connecting-pipes, at the places where the acid is siphoned off, &c. The wind must also be kept off, and any loose pieces in the bratticing round and between the chambers promptly put right; a gale of wind may tear off the straps of a whole chamber-side at once or force the frame to one side. The gangway round the chambers ought to be wide enough (say 5 feet) to admit of easy control and repair.

It used to be reckoned that with 6 lbs. lead in normal circumstances a chamber would generally last from eight to ten years, but with many repairs during the latter years. But since the art of building, and more particularly of *managing*, vitriol-chambers has become better understood, they have been made to continue much longer in use. On the Continent, where they are not (or formerly were not) so much strained as is frequently the case in England, vitriol-chambers generally last much longer than the above term, viz., 20 or even 30 years; but even in England this is found to be the case at some works where the chambers are built with more regard to durability than to economy in first cost.

There is no doubt whatever that, all other things being equal, a chamber lasts longer in proportion as it is less heated; it is not so much the heat itself, but the intensity of the chemical reactions going on within the chambers which produces the heat, and moreover the increase of the action of all chemicals by the elevation of temperature brings about the same result. It is only another way of stating this fact, if we say that a chamber lasts all the less time the more nitre is sent into it and the more acid is made in it.

In the case of chambers without a roof the top generally wears out first, then the parts dipping into the bottom-acid and the ends; the bottom remains good up to the last, unless nitric acid gets to it, which most easily happens in the last chamber, if its strength is allowed to run down too much.

When a chamber requires so much repairing and patching that it does not seem likely to pay, and when, after all, the escape of the gas from the too numerous chinks and rents can no longer be kept down, it is very bad economy not to pull it down at once; for the yield of acid must fall off very much. In this case a temporary connexion is made between the two apparatus on either side of it, the acid contained in the chamber is worked down as long as it will run, a hole is cut into its side, and men provided with india-rubber boots are sent in to shovel up the *mud* lying at the bottom into a heap, from which a good deal of acid is still obtained by draining. The mud must now be removed; if the space underneath is free, a receptacle is formed by low banks of clay, a hole is cut in the chamber-bottom, and the mud pushed down. If this is not possible, it must be removed in a much more troublesome manner, by thickening it with sawdust and washing with water. In either case it is dried in a reverberatory furnace, sometimes with the addition of a little lime in order to prevent the escape of acid vapours. Notwithstanding this, the operation usually causes a very disagreeable stench, probably owing to arsenic, selenium, &c. The dried mud, principally consisting of lead sulphate, is either smelted for lead in a small cupola heated by coke, or simply sold to the lead-workers.

After taking out the lead-mud, the chamber-lead is detached from the frame, and the good whole pieces rolled up for use as sheet-lead; the others are melted in an iron pan, the dross is scummed off, and the lead cast in the usual pig-moulds; at the lead-rolling mills this lead is much liked for other chemical purposes (see p. 431). Including the pig-lead, the dross, and the lead sulphate, usually nine tenths or upwards of the original weight of the chamber is recovered; the remainder has disappeared in one shape or another with the acid made.

If the frame has been substantially made, it stands a second, sometimes a third lead chamber, with a few repairs, putting in odd beams &c. Of course, in case of any doubt, it would be extremely bad economy to run the risk of having to stop a chamber because its frame would not hold out as long as the lead.

Mr. G. E. Davis has sent me the following observations:—A set of three chambers (20 x 18 x 120 feet) had been at work at high pressure for seven years, when the first two chambers were pulled down. They were built of 7 lbs. lead; at the end of the time the top was still between 5 and 6 lbs., the bottom between 2 and 3 lbs., the sides were almost *nil.* In the first chamber sulphate of lead equal to 19 tons metallic lead was found, in the second 16 tons metallic lead. The chamber-top had not been repaired all this time, the sides had had new lead all round, and the bottom had been repaired in places.

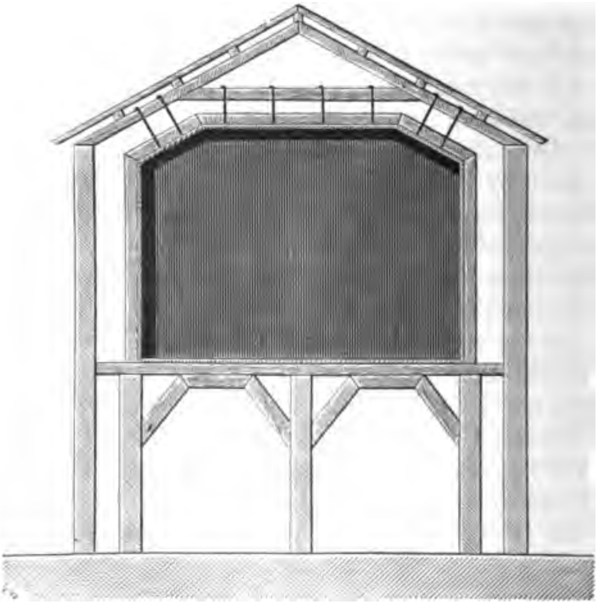
Special observations on the wear and tear of lead chambers have also been made by Burgemeister (Chem. Zeit. 1889, p. 1633). A set of two chambers was observed after 23¾ years, during which time the larger chamber had been at work with brimstone for 32 months, with pyrites (first Westphalian, then Rio Tinto) for 178 months, idle for 75 months. The thickness of the lead was originally 2·57 mm., at the end of the period on an average only 1·88, that is a loss of 0·69 mm. or 26·8 per cent. The part dipping into the bottom-acid was most worn; next the places where the lead was double or where it was protected against cooling by the wooden frame. For this reason it is best to burn the joints outside, because the inner part of the lap-joint is then eaten away first without injuring the joint; if the joint is burned inside, the lap is loose on the outside, and as soon as the inner part is eaten away the chamber must leak. The bottom of the chamber, which is protected by the acid, suffers least. A small chamber which was placed between the Glover tower and the large chamber, and which was kept at a higher temperature (from 65° to 90° C.), had lost in 120 working months as much as 17·65 per cent. of the thickness of lead.

Shape of Lead Chambers.

The *shape* of the chambers is nearly always that of a long box of square or approximately square transverse section. At some places, in order to save lead, the chambers have been made up to 60 feet wide; but this is not to be recommended on any account. It causes difficulties in constructing the wood frame, and, what is more serious, the yield of acid in such large chambers is not so good as in those of ordinary shape, say between 20 and 30 feet wide. This is easily understood, as in such very large sections the gases do not get properly mixed, and there are too few surfaces offered for contact and cooling (comp. Chap. VII.).

For the purpose of saving lead, the chambers belonging to the different works of the Rhenania Chemical Company are constructed in the way illustrated in fig. 176—that is, with the top corners cut off, to suit the slope of the roof. This admits of putting the largest possible height of chamber into a roofed building; and Mr. Hasenclever also contends that the "dead corners" of square-sectioned chambers are thereby avoided. There is also less wear

Fig. 176.



and tear than in the sharp corners of chambers of the ordinary square section (comp. p. 450).

The usual width of vitriol-chambers is rarely below 20 or above 30 feet; their height varies from 16 to 25 feet, or exceptionally a few feet more. Their length (always speaking of the principal chambers, not of the small chambers or "tambours" arranged before and behind these in the French system) is rarely below 100 feet, but may attain 200 or even 300 feet.

H. A Smith, in a pamphlet on the Chemistry of Sulphuric-acid Manufacture (1873), endeavoured to prove that the upper space of the vitriol-chambers did no work at all, and that chambers of 3, 6, or at most 8 feet in height would be most suitable. His experiments (described and refuted in detail in our first edition, p. 285 *et seq.*) were decidedly inconclusive, and a practical test of his theory at the Oker works led to its entire rejection.

E. and T. Deplace (E. P. 5058, 1890) describe an *annular* chamber, in which the gaseous current is continually changing its direction, owing to that shape. Siphon-shaped tubes placed on each side of the chamber produce a circulation and mixture of the gases. These chambers occupy less space than the usual form, and are stated to produce up to 6 kils. acid of 52° B. (=3·7 kils. H_2SO_4) per cubic metre=1 lb. sulphur to 13·2 cub. feet per 24 hours. A few sets of this kind have been erected in France and England. According to the 28th Alkali Report, p. 55, the shape of chamber actually built differs a good deal from that described in the patent. According to information received from manufacturers, the production from these chambers per cubic foot does not exceed those of ordinary chambers.

Th. Meyer's "tangential chambers" (E. P. 18,376, 1898) are also devised as a means for inducing a better mixture of the chamber-gases. The chambers should have a circular or polygonal section, and the gas inlet-pipes be placed tangentially on the upper part of their sides, the outlet-pipes in the centre of the bottom *. This imparts a spiral motion to the gases, rapid at the circumference, slower towards the centre, and thus causes them to travel through a greater distance and to get much better mixed than in ordinary chambers. The inventor gives more details

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* The patent specification speaks of the centre of *the ceiling*, but in practice the gas-exit is from the centre of the chamber-*bottom*.

concerning his system in Chem. Zeit. 1899, p. 296; Zsch. angew. Ch. 1899, p. 656, and *ibid.* 1900, p. 739. His system has been carried out at the Norddeutsche Chemische Fabrik, Harburg, and at the Chemische Düngerfabrik, Rendsburg. The chambers are 10 metres in diameter and 8 metres high, in a set of three, with Glover and Gay-Lussac towers. The draught is very good, the yield from 92·5 to 95·2 of the theory (291 H_2SO_4 per 100 S burned); per cubic metre the production is from 3·66 to 3·87 kils. H_2SO_4, with a consumption of 1·34 to 1·44 nitric acid 36° B. (=1·0 to 1·07 nitrate of soda) for 100 H_2SO_4, or, say 3 $NaNO_3$ to 100 S burned.

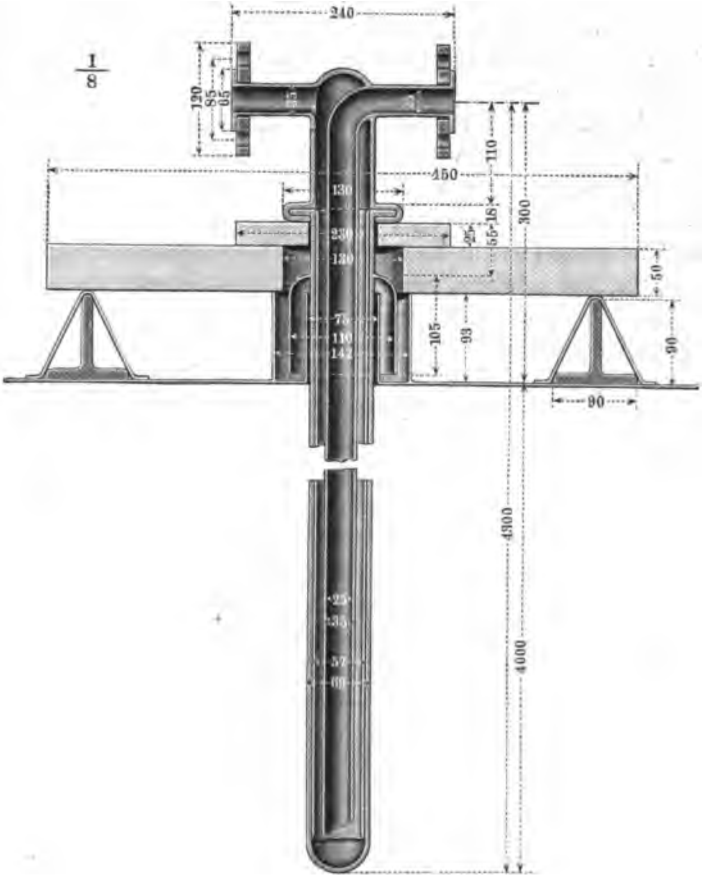
[This production is good, but still inferior, not merely to French "forced work" with ordinary chambers, but also to that of some of the German works, comp. p. 468.]

Recently (Zsch. ang. Ch. 1900, p. 742) Meyer has improved his chambers by arranging in the first (and hottest) chamber a *cooling system,* consisting of 43 lead pipes, 2 to 2½ inches wide, suspended in water-lutes from the chamber-top all round the circumference and reaching 8 to 10 feet down into the chamber. They are closed at both ends; through their tops enter thin lead pipes, reaching nearly to the bottom of the larger pipes, for introducing the cooling-water, as shown in fig. 177. The whole offers a cooling-surface of 23 square metres (=250 square feet), *i. e.* 7 per cent. of the heat-radiating surface of the chamber sides and ceiling. The water, of which 8½ tons is used per day, issues at a temperature of 67° C. The heat evolved by the process of converting SO_2, O, and H_2O into H_2SO_4, as far as it goes on in that chamber, is calculated =2½ millions metrical heat-units per 24 hours, of which 500,000 are removed by the cooling-water =20 per cent. This is not shown by the chamber thermometers, as the loss of heat is made up by that newly generated by the chemical process, and it is manifested by the increased production of sulphuric acid (according to the theories of Lunge and Sorel, comp. later on). The pipes last a long time and can be immediately renewed by taking them out of the hydraulic seals. The hot water is used for feeding the steam boilers.

I have shown in Zsch. f. angew. Ch. 1902, pp. 151 *et seq.*, that the advantages to be realized by Meyer's proposals by his own showing are not very considerable. It is very doubtful whether for equal weights of lead his tangential chambers produce any more than even moderately well-managed ordinary chambers.

In another paper (Zsch. angew. Chem. 1901, p. 1245), Meyer acknowledges the "Lunge towers" as the best solution of the problem of bringing the *misty* particles floating in the chamber to act upon each other, and he advises to combine such intermediate towers with his "tangential" chambers.

Fig. 177.



I am informed that in 1902 serious attempts had been made to introduce circular chambers into England, but after inquiry and consideration this plan was given up.

Combination of chambers to sets.—Sometimes the whole working-space is contained in *one* chamber. Scheurer-Kestner (Wurtz, Dict. iii. p. 147) mentions a single chamber of 142,000 cubic feet capacity, and quotes the experience of different works, according to which it is quite unnecessary to divide the set into several chambers. More frequently, however, several chambers are combined to form a set, which, to begin with, affords this advantage —that for repairs it is not necessary to stop the whole set.

A great diversity of opinion exists as to how the single chambers are to be combined to form sets. Among the hundreds of vitriol-works very few will be exactly alike in this respect; and frequently even in the same works different combinations are found. We may, however, consider it as established that it is almost indifferent in which way the chambers are combined, if they are, in the first instance, properly built (that is, not too high or wide), and if, secondly, they possess a certain cubical capacity for the quantity of sulphur or pyrites to be consumed. Within these limits those combinations are best which require least lead, and which are laid out so as to afford the greatest facility for supervision. Of course there is also an extreme limit to the capacity of the whole set; but opinions differ upon this point also. At some works a set consists of nine or eleven chambers of 35,000 cubic feet each; at others, equally large, it is limited to three chambers of 42,500 cubic feet each, &c. Thus at Hebburn-on-Tyne several sets of three chambers each are employed, each chamber 20 feet wide, 125 feet long, 17 feet high on one side, 18 feet on the other; each set serves for 18 burners, burning 7 cwt. daily. At Gateshead there are several sets of three large chambers, each so arranged that two of them communicate separately with a set of kilns ("working-chambers"), and both of them are connected with the third chamber; the whole set has a capacity of about 200,000 cubic feet. More usually the gas passes through all three chambers in succession. Very often four chambers are combined, each of them about 20 x 20 x 130 feet,—or five chambers, two of them working-chambers, thus, $\begin{matrix}1-3\\2-4\end{matrix}\!>\!5$,—or even six chambers, thus, $\begin{matrix}1-3\\2-4\end{matrix}\!>\!5-6$.

In America (Zsch. f. angew. Chem. 1894, p. 133) I found at one place a set of twelve chambers of equal size, each 24 feet long, which, it was asserted, combined very good yield with small consumption of nitre. At another place they had three chambers, 60, 50, and 40 feet in length, with plate-columns between.

The chamber-set described by Hasenclever (Chem. Ind. 1899, p. 26) consists of two very large and two small back chambers of a total capacity of 7250 cub. met. =267,000 cub. feet. He mentions the existence of sets comprising 12,000 cub. met. =420,000 cub. feet, which form decidedly a very undesirable exception.

At one of the most modern German works I found sets consisting of three chambers, all of them 10 metres wide and 7 metres high; the first had a length of 41, the second of 31, the third of 10 metres. They produce 2·8 kils. H_2SO_4 per cub. metre (equal to about 18 cub. feet chamber-space per lb. of sulphur burnt in 24 hours).

The Rhenania Chemical Co. prefers throughout sets of two equally large chambers, followed by two small back chambers (1902).

In France it is usual to combine three chambers in a set, exceptionally four or five. The total capacity of a set hardly ever exceeds 6000 cub. metres (=210,000 cub. feet).

According to Mon. Scient. 1900, p. 563, Benker has for a number of years built chambers (in France) on the following plan:—Besides the Glover tower he employs a dry filtering chamber in order to retain flue-dust and arsenic. His chambers are three in number, of a total capacity of only 2000 to 3000 cub. met. (70,000 to 105,000 cub. feet). Into the last of these he introduces SO_2 (burner-gas); then comes a small intermediate chamber and then two Gay-Lussac towers. The draught is produced by a fan-blast. Benker claims to produce 6 to 7 kils. acid of 52° B. (=3·7 to 4·3 kils. H_2SO_4) per cubic metre (=1 lb. sulphur burnt upon 13·2 to 11·3 cubic feet!), with a consumption of 0·8 to 1·0 nitric acid 36° B. per 100 acid of 52° (=3 to 3·7 lbs. $NaNO_3$ per 100 S burned). The chambers are fed with a water-spray in lieu of steam (*vide infra*), and he always injects some SO_2 (burner-gas) into the last chamber (G. P. 88,368 & 91,260; comp. later on).

Benker, according to direct communications received from him in 1902, employs only narrow chambers, say 18 to 20 feet wide, and from 25 to 33 feet high. Such chambers are, in the first instance, better adapted for water-spraying, but they also afford a better mixture of the gases, especially if the sides are cooled, by employing an open bratticing for the side passages (2½ in. laths with 1½ in. clear spaces) and a roof-rider. The cold gases descending along the sides must rise again in the centre; but in the case of very wide chambers a dead space remains where the velocity is very slight, and where the mist of nitrous vitriol sinks down without acting on the gaseous constituents. This cannot produce "high-pressure work" (comp. later on). Benker objects to *Meyer's* tangential chambers that there is no question of tangential action, that in the centre of these circular chambers gases of very different concentrations get mixed up, and that they would be too expensive if the only proper way was followed, viz. building many small circular chambers in a set. We shall later on, when describing the system of water-spraying, give a complete diagram of Benker's chambers.

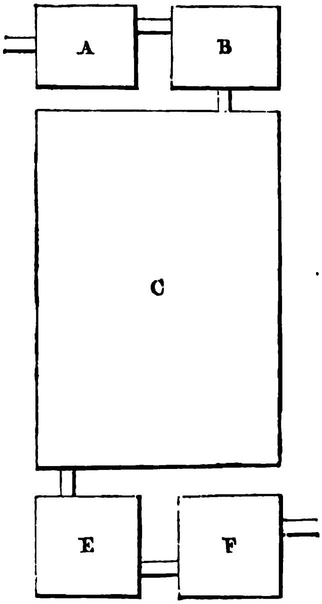
The *size of the chambers* varies very much. Apart from the "tambours" of the French system, the proper chambers are made with as little as 10,000 and as much as 140,000 cubic feet capacity. Such small chambers are no longer built as main chambers; the usual capacity of these may now be taken as ranging from 25,000 to 70,000 cubic feet, more frequently nearer the upper than the lower limit. Smaller chambers cost much more, comparatively, than large ones, and it is doubtful whether they afford any corresponding advantages.

The different chambers of a set are either placed on the same level, or, more suitably, each following chamber is placed 1 or 2 or, better, 3 inches higher than the preceding one, so that the acid of the back chambers can be run more easily into the working-chamber. In the first chamber the acid is both strongest and most free from nitre; and it is therefore preferable to draw off any acid from this, whether it be for sale, for use, or for concentration. The acid drawn off is replaced partly by that newly formed in the same chamber, partly by the weaker acid run over from the other chamber. If there is only one long chamber, the acid is always found strongest near the entrance of the gas.

In England, all the chambers of a set are generally of equal size, apart from local circumstances; and this plan is now more frequently found on the Continent as well than formerly, when the French system, even now the more usual, was the only one to be met with. In this system there is a "large chamber," C (fig. 178), placed at the lowest level, combined with a few small chambers at a higher level, both before and behind the large one. Thus the first small chamber or "*tambour,*" A, serves for denitrating the nitrous vitriol by hot water; the second one, B, for introducing fresh nitric acid; the third and fourth tambours, E and F, for finishing the reaction.

In the south of France (Favre, 'Monit. Scient.' 1876, p. 272) there is mostly a large chamber of 135 × 26 × 20 feet, or of 100 × 16 × 22 feet, combined with two small chambers, together about 140,000 cubic feet. At Aussig each large chamber is 200 feet long and 24 feet wide, and is combined with a small tambour for catching the fine dust, and two small end chambers, not receiving any steam, but only serving for cooling the gas previously to its entering the Gay-Lussac tower.

Fig. 178.



Some manufacturers reject all preliminary chambers (tambours), because the chamber process is carried on best if a large space is afforded at once for the mutual reaction of the gases. Thus in a large French works two thirds of the whole chamber-space are occupied by the first chamber, two ninths by the second, and one ninth by the third; this system is also adopted at Uetikon.

At the Government works at Oker (official communication, 1902) there are five sets of chambers, the best working of which have the following dimensions:—

Chamber	I.	35 met. long,	8·00 m. wide,	6·50 m. high	=2860	cub. met.
„	II.	30 „	8·00 „	6·50 „	=1560	„
„	III.	30·15 „	5·49 „	5·25 „	= 869	„
					5289	

The chambers communicate by pipes 1 met. wide, entering about $\frac{2}{3}$ of the height and leaving 1·20 above the bottom. Small front and back chambers have been designedly left out in this system, but small back chambers exist by chance at the older sets.

Small chambers, of course, require more lead and space than large ones of equal capacity. A preliminary chamber, however, is serviceable, where no Glover tower is present, for catching the dust and cooling the gas, so as to save the large chamber. For the same reason the nitric acid was once usually introduced into a special tambour; but it is best, as we shall see, to run it down the Glover tower.

A small chamber at the exit end is certainly serviceable for drying the gases previously to their entering the Gay-Lussac towers in cases where there is no long tube or tunnel for the above-named purpose.

The waste of lead in small chambers is more easily understood by a definite example:—A chamber of 100 × 20 × 20 feet has a cubical capacity of 40,000 cubic feet and a surface of 8800 square feet. A tambour of 16 × 10 × 10 feet has a capacity of 1600 cubic feet and a surface of 840 square feet. Its contents are therefore $\frac{1}{25}$, but its surface almost $\frac{1}{10}$ of that of the large chamber; and consequently its surface is nearly 2½ times as large, in comparison with its capacity, as that of the large chamber.

Whilst, of course, there is no doubt that a given cubic space of chamber-room is more cheaply obtained with a few large than with a greater number of small chambers, it is, on the other hand, very easy to overstep the mark in this direction. We have seen above that, in the case of chambers of an excessive section, the gases do not get properly mixed; but the same principle applies even to the division of the chamber-space in the direction of its length, since every time the gas has to be compressed into a comparatively narrow connection-tube in order to pass from one chamber to another, this must bring about a good mixture superior to that produced in the same length of undivided chamber-space. For this reason, to begin with, it seems expedient to subdivide the chamber-space by multiplying the number of chambers; and we shall further on meet with another strong reason for the same purpose, namely, that the cooling down of the contents of the chamber, essential for the reaction among them, is promoted by their contact with the comparatively cool end-walls of the chambers.

In England it is taken as a practical rule that for every cubic foot of chamber-space there should be about 0·2 foot of total surface (top, bottom, sides, and ends). A chamber 20 × 25 × 100 feet would contain 50,000 cubic feet and have a total surface of 10,000 square feet, which is exactly the above-stated proportion. Sets of chambers in England are rarely made larger than 200,000 cubic feet; if more is required, the whole is broken up into two or more sets.

When speaking here, and elsewhere, of "chamber-gases," we always comprise in them not merely the *vapours* of water, nitrous anhydride, &c., but also the *misty* particles of liquid sulphuric acid, nitrosulphuric acid, &c., floating about in the atmosphere of the chambers.

Schertel, in fact, starting from the principle adduced by my experimental and theoretical basis, to which he agrees, proposes to multiply the number of chambers, keeping them rather short (Chem. Ind. 1889, p. 80). Bode (Zeitsch. f. angew. Chemie, 1890, p. 11), on the same principle, proposes chambers of half the usual length, but twice the ordinary width—say 40 feet. This would involve some difficulties, although not insuperable, in constructing the chamber-frames. Later on (Sächs. Jahrb. 1890, p. 148) Schertel described practical experiments bearing out the theoretical considerations just mentioned; and further experiments on the manufacturing scale, entirely confirming my own results and conclusions, have been made by Retter (Zeitsch. f. angew. Chem. 1891, p. 4).

In the usual case, where a set of several chambers is combined to form the acid-making apparatus, the question arises how the single chambers of the set are to be connected. One thing about this is certain: that the *connecting-tubes* must be placed at the small ends, so that the gas shall travel right through the length of the chambers, and no dead corners are left. But the next question is, at what part of the section the connecting-tubes are to leave or enter the chambers. There is general consent as to this, that the gas should enter the first chamber near its top. Some proceed in this way: they take the gas away at one end near the bottom and introduce it into the next chamber near its top. Others maintain just as strongly that this is wrong, and that, on the contrary, the gas-pipe ought to leave each chamber near its top and enter the next chamber near its bottom. Others, again, contend that it matters very little where the gas enters and leaves, and that it is therefore the simplest plan to make straight connecting-tubes about midway in the height of the chamber. This last view seems to be borne out by the practice of several practical men of very large experience, and it agrees very well with the investigations of Lunge and Naef (*vide infrà*), who found that the composition of the chamber-gases in any given cross-section of the chambers does not differ very materially between top and bottom, so that it must be indifferent where the connecting-tubes are placed. This is confirmed by information from the Rhenania works in 1902.

The connecting-tubes may be round pipes or angular flues (tunnels). The former are preferable, because they can be made without a frame, and because they stand better. They must, however, be made of strong lead, say 9 to 12 lbs. per square foot, and bound here and there with iron hoops, between which and the lead wooden staves are placed in order to keep the pipes in shape; but if the weight of the lead amounts to 15 lbs. per square foot, no staves are needed. Figs. 179 & 180 will make this clearer.

The iron hoops serve also for suspending the pipes from beams &c. The *width* of the pipe introducing the gas into the first chamber, whether it comes from the Glover tower or from the burners, must be adapted to the quantity of gas conveyed. For a combustion of 7 tons pyrites daily a pipe of 2 feet diameter, for 9 tons one of 2½ feet, upwards of that one of 3 feet diameter will do; more than 10 tons are rarely consumed for a single set in twenty-four hours. Since the volume of the gas decreases in its onward journey, the connecting-pipes between the single chambers may be successively a little smaller; but it is not well to grudge any thing here, since no harm is done if the pipes are too large, but very much if they are too small.

Fig. 179.

Fig. 180.

At Griesheim several connecting-tubes are introduced between the chambers instead of one. This seems very rational, and at the same time serves for partially cooling the gases in their transit, which we shall find further on to be an important feature. "Dead corners" are most easily avoided by this plan.

The total *cubical contents* of a set of chambers must bear a certain proportion to the quantity of acid to be produced, several special circumstances modifying that proportion. Thus it is certain that for pyrites more chamber-space is needed than for sulphur; we have seen above (p. 400) that the relative proportion may be stated as 1 : 1·314. But now the question is, What is the absolute amount of space needed? Properly speaking, the connecting-pipes, if they are of great length, and the Glover and Gay-Lussac towers should also be included in the calculation, and that to a larger extent than corresponds to their cubical contents.

The consumption of nitre also influences the chamber-space; within certain limits a larger consumption of nitre may compensate for a smaller space.

Partly from this the widely divergent views on this point may be explained, but not entirely; for some manufacturers obtain about the same yield as their neighbours possessing half as much more chamber-space, although both the pyrites and the general construction of the plant and their consumption of nitre are as nearly as possible the same. In the following remarks we shall reduce all measures to cubic feet of chamber-space required for burning 1 lb. of sulphur daily, taking, in the case of pyrites, the sulphur bought, not that actually burnt.

For some particulars concerning older methods, comp. 2nd edition of this work, pp. 371 & 372; for recent ones, pp. 456 & 458. From sundry English alkali-works I can state the following proportions (1879):—

I.	II.	III.	IV.	V.
28	25	20	18	16 cubic feet.

I. and II. were considered too high by the chemists of the respective works themselves; but it should be stated that the same space was employed in 1864, when 30-per-cent. Irish pyrites was used, for which it was more suitable. III. (viz. 20 lb.) is a proportion employed at many large works; but IV. and V. are found in works having as good a yield of acid (270 to 288 o.v.) and no larger consumption of nitre (3½ to 4 per cent.). In all cases rich Spanish or Norwegian ore was burnt, and both Gay-Lussac and Glover towers were used. From this it follows that under the same conditions 20 cubic feet per lb. of sulphur charged is amply sufficient, and 18, or even 16, will do; but the latter certainly is generally assumed to be the lowest allowable limit. This agrees with a statement of Wright's (Chem. News, xvi. p. 94), who demands 16 to 19·2 cubic feet.

From the Inspectors' Alkali Reports it will be seen that the amount of chamber-space actually employed at English works varies in a most extraordinary way, and not merely in consequence of the fact that very small works generally employ an excessive chamber-space. It is also seen from the same source that the usual assumption that less chamber-space is used with brimstone than with pyrites is altogether erroneous. We will here give merely a few figures obtained by taking averages of the single works enumerated, leaving out those burning both pyrites and brimstone, or coal-brasses, or "oxide."

In the 20th Report, pp. 48 & 49, we find the average of 18 works burning pyrites to be 23·1 cubic feet of chamber-space (minimum 15·5, maximum 38·4); the average of 10 works burning brimstone 29·7 cubic feet (min. 21·7, max. 44·8). In the 21st Report, pp. 20 & 21, 21 works burning pyrites average 26·6 cubic feet (16–40); 15 works burning brimstone average 26·2 cubic feet (21–48). On pp. 64 & 65, 22 works burning pyrites average 29·2 cubic feet (17·3–43·2); 18 works burning brimstone average 31·4 cubic feet (19·3–46·2). But as the great majority of these works are too small to afford a real guidance in this respect, we will quote in detail (from 21st Report, p. 81) the figures of fifteen medium and large-sized works in the Widnes district, comprising some other interesting information:—

Pyrites burnt per week. Tons.	Cubic feet chamber-space per lb. of S burnt in 24 hours.	Nitrate of soda per cent. of sulphur burnt.	Capacities of Gay-Lussac towers per ton pyrites used per week. Cub. ft.	Total acidity of waste gases as grains SO_3 per cub. ft.
175				
52	21·0	3·50	……	……
350	18·0	5·00	65·8	0·87
210	17·8	4·70	18·7	2·10
125	28·0	4·00	36·1	0·65
98	17·8	4·20	32·4	2·88
240	21·0	4·25	24·0	1·71
250	28·3	3·75	15·7	2·34
150	21·0	……	37·8	0·79
250	19·3	5·00	20·5	1·90
60	22·3	……	27·5	3·89
260	22·0	3·30	33·7	1·60
117	21·0	4·00	53·5	1·30
183	20·0	……	21·5	2·94
70	17·5	……	79·6	0·70
Total and averages 2590	21·0	4·17	44·4	1·82

The usual proportions in the south of France were stated by Favre (Monit. Scient. 1876, p. 271) as follows:—Each square metre of grate-surface in the pyrites-burners daily receives 270 kilograms of 40-per-cent. pyrites, and corresponds to 180 cubic metres of chamber-space. This means 1·66 cubic metre for each kilogram of sulphur charged, or 26·5 cubic feet per lb.

In the north of France I found, in 1878, about 8 cubic feet per lb. of pyrites, or about 17 cubic feet per lb. of sulphur charged, with good yields and low consumption of nitre, but only for low or medium temperatures; in summer ¼ to ⅓ more chamber-space is required.

Recently a new style of working has been introduced into several French works, called "*production intense*," say "forced or high-pressure work." It consists in supplying the chambers with a greatly increased stock of nitre, without losing any of it, by means of largely increased Gay-Lussac and Glover towers; in this way the production may be increased to almost twice the usual amount, so that, in winter at least, a maximum of yield and a minimum consumption of nitre are attained with the extremely small chamber-space of 0·7 cubic metre per kilogram, or 11·2 cubic feet per lb. of sulphur burnt. We shall have frequent occasion in later parts of this book to speak of this "forced style," which at the time of writing is nowhere practised in England or Germany.

In 1900 Pierron (Monit. Scient. 1900, p. 367) stated as a *minimum* production in 24 hours, 2·34 kils. $H_2SO_4 = 0·78$ kils. sulphur burned per cub. met. = 1 lb. S per 19 cub. feet, but at Kuhlmann's works the normal production is 2·9 kils. H_2SO_4, and Benker (p. 459) claims obtaining 3·6 to 4·2 kils. H_2SO_4 with ordinary chambers. The ordinary production can be increased by the use of artificial draught (fan-blasts), by "tangential chambers" (comp. p. 456), by "plate columns," and by other means described in their places.

For Germany, Niedenführ (1902) states the usual cubic space = 1·2 cub. met. per kil. of sulphur = 19 cubic feet per lb., which is just the same as the *maximum* space allowed in France, but decidedly more than the average employed in that country, even where no "intense production" is aimed at. But Niedenführ's statement is decidedly not valid for the most carefully managed German works, which, according to direct information, manufacture 3·5 H_2SO_4 per cubic metre of chamber-space, which is about 0·85 cub. metre per kil. of sulphur burnt or about 14 cubic feet per lb.

For the Rhenania works, producing their SO_2 from zinc-blende, Dr. Hasenclever states as the normal production 2·5 kils. of 60° B. per cubic metre in 24 hours, with a consumption of 0·5 to 1·0 per cent. nitre per 100 acid of 60° B.

The following (hitherto unpublished) data have been kindly supplied to me by Mr. G. E. Davis respecting the results obtained in a set of three chambers, each 120 × 20 × 18 feet, with a Glover 8½ × 22 feet and Gay-Lussac 12 × 12 × 60 feet. This set was worked:—A. One month without the towers: pyrites burned 135 tons, potted 96 cwt., 25 cb. ft. chamber-space per lb. of sulphur in 24 hours; 79 lbs. nitrate of soda sent into the chambers per ton of pyrites. B. One month with the towers in full operation: pyrites burned 180 tons (19 cb. ft. chamber-space per lb. sulphur), 101 cwt. $NaNO_3$ introduced by Gay-Lussac acid, 56·2 cwt. nitrate potted, 98 lbs. nitrate introduced into chambers per ton of pyrites. C. One month with towers: 240 tons pyrites (=14·4 cubic feet per lb. sulphur), 205·6 cwt. $NaNO_3$ in Gay-Lussac acid, 86 cwt. nitrate potted, 135 lbs. nitrate in gases per ton of pyrites. D. One month with towers: 302 tons pyrites (=11·5 cub. ft. chamber-space per lb. S), 277·3 cwt. $NaNO_3$ in Gay-Lussac acid, 135·1 cwt. potted, 152 lbs. total nitrate per ton of pyrites. Lastly, E. One month with towers: 380 tons pyrites (=8·1 cb. ft. chamber-space per lb. S), 394 cwt. $NaNO_3$ in Gay-Lussac acid, 203 cwt. nitrate potted, total nitrate 176 lbs. per ton of pyrites. Under the last conditions the chambers were worked for nearly a year; oxygen at burners 10 per cent., at dust-burner 12 per cent. Average acidity of gases going into Gay-Lussac 5·5 grains H_2SO_4 per cubic foot, and gases leaving the tower 1·4 grains H_2SO_4.

The *yield* varied very little in all these cases, viz. from 40·2 cwt. acid of 123° T. per ton of pyrites in A to 39·8 cwt. in E. (The above quoted consumption of nitre is very high, even for easy work, let alone for high-pressure work.)

Mr. Davis states the general opinion of English acid-makers as follows:—"If you go on in the old way, working with 25 cubic feet of space per lb. of sulphur per 24 hours, the process goes on absolutely by itself. Decrease your chamber-space to 15 cb. ft., and you want a chemist and clever foreman, while with 8 cb. ft. neither foreman nor chemist knows what peace is either by night or day."

The preceding statements refer to ordinary pyrites, but when acid in a given chamber-space than usual is the ***employment of a very large quantity of nitre*** (***intense production, or high-pressure work***). This means providing the chambers with unusually large Gay-Lussac and Glover towers, which absorb a considerable portion of the saving in the size of the chambers themselves. Still, this style of work has obtained much favour in France, where it has led to a sensible reduction of the chamber-space at some works, as already mentioned (p. 468). But it is evident that the limit of reduction by that means is soon reached.

A third way of increasing the production of acid for a given chamber-space is by *contrivances for a better mixture of the gases within the chambers.* Some of the proposals in this direction are combined with the *cooling action* demanded by the theories to be explained in Chap. VII.

Most proposals for manufacturing sulphuric acid in a diminished space start upon the assumption that in the ordinary vast chambers the gases are not sufficiently well mixed ; some of them also on the supposition that there is not enough "condensing" surface for the sulphuric acid, and that this should be artificially increased. So far as it was assumed that the sulphuric acid required to be condensed from a vapour into a liquid, similar to the condensation in distilling alcohol, &c., this theory is, of course, wrong, inasmuch as the sulphuric acid is liquid as soon as formed, and does not exist at all in the chambers in the state of vapour. But we shall see further on that for other reasons it is certainly true that a large amount of *surface*, for the chamber-gases to impinge on, is indeed a most important factor in the chamber-process, and that, moreover, a certain amount of *cooling* is also of great importance in this respect. We shall see that this proceeds from the necessity of bringing about the reaction between the nitrososulphuric acid and the liquid water or dilute sulphuric acid floating about in the chamber. Whilst, therefore, we must acknowledge that former inventors were on the right track when increasing the surfaces of contact, it is a fact that their efforts were unsuccessful; but this was caused by the circumstance that they did not (and could not in the then state of the subject) properly understand the essence of the process, and that they consequently chose the wrong means for their ends. Partitions within the chambers, if made of lead, are most quickly corroded; if made of glass, they soon collapse (*vide* p. 474).

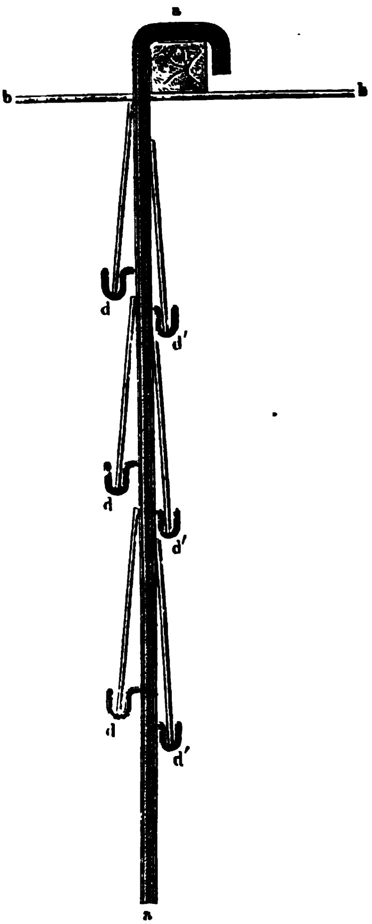
An arrangement of Ward's (E. P. 1006, of 1861) consists in a kind of mixing-chamber, for the combustion of 7 tons pyrites in twenty-four hours, 64 feet long, 16 feet high, and 20 feet wide, followed by a second lead chamber, or flue, 200 feet long by 3 feet high and 3 feet wide, almost filled up with sheets of glass to a length of 25 feet. The sheets lie in a horizontal position, and are kept a little apart by strips of glass, to permit the passage of the gases. Ward believed that upon these sheets (in lieu of which tubes might be used) nitrous vitriol would condense and afford a large surface to sulphurous acid. His plan does not appear to have been carried out in practice, or if it was it must have been abandoned again, probably because his erection possessed too little stability or was too easily stopped up. The horizontal arrangement is also unfavourable to a systematic action of the gaseous and liquid agents, for which streams in opposite directions (up and down) are preferable, as we shall see below; and the total lack of a cooling arrangement would make the whole principle of reaction on the solid surfaces incomplete, as will be proved later on.

Mactear (Journ. Soc. Chem. Ind. 1884, p. 228) has carried out some experiments showing the importance of surface condensation. A tray, placed in a vitriol-chamber, one square foot area, was found to give 708 grams H_2SO_4 in 24 hours. By placing in the tray 12 pieces of glass, 12 in. by 6 in. each, in a vertical position, the amount of acid obtained in 24 hours rose to 1644 gr., or 2·3 times as much, and by placing the glass slips horizontally, the same distance apart as before, the acid rose to 3226 gr., or 4·5 times more than without the glass. Other experiments made with "surface condensers" within the chambers showed that in the case of flat vertically placed sheets the side facing the gaseous current condensed more acid than the opposite side, in the proportion of 100 : 78. When the same plates were placed horizontally, with their edges facing the curreut of the gases, the amount obtained from the double surface was 172, against 178 in the former case.

The principle of surface condensation is also employed in de Hemptinne's chamber-system, which will be mentioned in the 9th Chapter, in connection with his system of concentration.

At some places, *e. g.* at Uetikon near Zurich, there existed for a time a peculiar kind of chambers. Each set consisted of only one large chamber, 330 feet long; within this, however, there were two partitions, dividing it really into three chambers. The partitions are made as shown in fig. 181. A row of perpendicular iron gas-tubes of 1-inch bore, covered with lead, *a*, is placed across the chamber, carried through its top, *b*, and hung from one of the joists *c*. At vertical distances of 2 feet there are lead hooks, *dd*, attached to the tubes, on the opposite side other hooks, *d' d'*, a little lower. These hooks must not be made of sheet-lead, because they bend too easily, but they must be cast. On these hooks sheets of glass 2 feet + 2 feet 6 in. are placed loosely, leaving chinks of about 1 inch width for the passage of the gases, in order to mix them better. These partitions do not seem to offer any guarantee of durability; and in fact, both at Uetikou and at other works, formerly possessing similar glass partitions, they have been removed again; they are said to have sometimes suddenly collapsed and cut through the chamber-bottom.

Fig. 181.



The simplest kind of internal partition, a lead one, is not practicable, because the lead, exposed to the heat and the gas on both sides, is very quickly worn away. This entirely disposes of the suggestion of Bornträger (Chem. Ind. 1885, p. 386) to make nearly horizontal (rather slanting) partitions in the chambers, in order to multiply contact-surfaces. Both in this case and in the Uetikon plan the internal contact-surface, not being cooled, does very little service (comp. later on).

Walter and Boeing (Germ. pat. 71,908) employ hollow partitions, made of acid-proof material, arranged across the whole width of the chambers. Double walls are constructed of such a form that the principal gaseous current enters through large holes near the bottom, rises upwards in the space between the walls, and issues at the top; at the same time the gases are allowed to penetrate into the inner space by numerous small openings, and to issue in the same way on the other side, so as to produce a good mixture. Buttresses and binders produce sufficient stability without interfering with the draught, which is also procured by making the sectional area of the openings and joints much larger than that of ordinary connecting-pipes. [This system aims at attaining the same object as the previously introduced plate-columns in a simpler way and without interfering with the draught. But, in consequence of the many outlets offered to the gases, it is doubtful whether they will travel exactly in the desired path. The stability of such inner walls, even when made of the best material, is very doubtful indeed, and a collapse must produce most disastrous results, as has been found in practice, wherefore the use of these partitions has been abandoned. They remind one of the plan shown, p. 474.]

Brulfer (French pat. 220,402) also employs hollow brick partitions within the chambers; he adds dividing apparatus, made of lead tubes with air-cooling, fixed behind each partition. When the gases have passed through a cooled divider, they again pass through a hollow brick divider.

A similar principle, in which, however, the idea of mixing the gases was the chief aim of the inventors, is involved in the proposal made by Gossage and many others, and frequently carried out in practice, of filling the chambers partially or entirely with *coke*, or of erecting special coke-towers at the end of the set, not as Gay-Lussac towers, but to be merely moistened by water or steam. In practice it has been found that even as a matter of construction this plan gave much trouble, because the great weight pressing upon the outside layers of the coke makes it bulge out or even cut through the chamber-sides. But apart from this it was found that the yield of acid for a given chamber-space was *not* increased, that more nitre was used, and that the acid was rendered impure by the coke. Everywhere, therefore, the coke has been removed again from the chambers themselves, and has been relegated to its legitimate place in the Gay-Lussac tower. The cause of this failure is probably two-fold: firstly, the injurious action of the coke on the nitrous gases, which would thereby be reduced with formation of carbonic acid (comp. Chap. VI.); secondly, the lack of any cooling, just as in Ward's case.

The same objections hold good for the apparatus of Verstraet (Bull. Soc. d'encourag. 1865, p. 531), which was worked in Paris for some time, but had to be abandoned as impracticable. It consisted of a number of stoneware jars without a bottom, covered 430 square feet of ground, cost only £280, and was to supply daily a ton of sulphuric acid of 106° Tw. There were twelve perpendicular stacks of five jars each, filled with coke and traversed by the burner-gas; nitric acid ran down over one of them, meeting the sulphur dioxide; and the resulting acid was run over the other stacks in regular rotation.

The apparatus of Lardani and Susini (Bull. Soc. Chim. viii. p. 295) is founded on the same principle. Its peculiarity is a "reaction-apparatus," whose lower part is filled with sulphuric acid, on the top of which a thick layer of nitric acid is floating; the upper part, divided from the lower by a perforated partition, is filled with pumice; the nitre-gas is regenerated to nitric acid by an excess of air and water in a system of pipes filled with pumice or coke.

That mixing the gases alone is not sufficient is proved by the small success of Richter's apparatus (G. P. 15,252), consisting of a steam-injector on the top of the chamber, which aspirates the gases from the lower part of the chamber and re-introduces them at the top. It is true that by this apparatus probably only a small portion of the gases would be set into circulation; otherwise the draught would have been interfered with in an intolerable way. At all events no great advantage has been obtained by using it in all the factories visited by me; but at some places a certain improvement is said to have been produced by this means.

The same proposal has been made in a somewhat modified shape by N. P. Pratt (E. P. 4856, 1895). He places a fan or steam-injector in front of the chamber, and a tower, fed with weak sulphuric acid, at the end of the chamber, the gases issuing from the top of this tower being re-injected into the chamber by means of the fan. Baffling columns may also be placed within the chamber. Modifications of this system by the same inventor are contained in the U.S. P. 652,687 to 652,690 and E. P. 10,757, 1899.

The Meyer's "tangential chambers" also belong to this class of apparatus (comp. p. 455).

Dr. Burgemeister (private communication) proposed both to *mix and to cool* the gases by arranging a number of lead pipes, 15 to 18 inches wide, vertically between top and bottom of the first chamber, and cooling these by air passed through. This plan is hardly practicable, as the immense extension of joints, especially at the bottom, will cause too many interruptions for repairs, but it can be more easily carried out, according to Hartmann (Chem. Zeit. 1897, p. 877), by constructing these inner pipes or shafts in the same manner as an ordinary chamber-bottom, that is with a hydraulic lute, formed by turning up the chamber-bottom round the bottom of the pipes. Hartmann employed a number of such shafts, 5 × 6 feet wide, from which he found an increase in the production amounting to 20 per cent., viz. 0·9 to 1·0 cub. metre chamber-space per 1·0 kil. sulphur burned. [This is not particularly high.]

F. Blau (G. P. 95,083) injects a spray of cooled sulphuric acid into the first hot part of the lead chambers, in order to keep down the temperature, and a spray of hot acid into the last part of the chambers where the reaction is sluggish and is to be revived in this manner. If the exit-gases thereby become too hot, they are cooled by a spray of cold acid before entering the Gay-Lussac tower.

A fourth way for increasing the production of acid is the employment of special *mixing and cooling towers and columns* between the chambers, even to the exclusion of all chambers except a first and perhaps a last small chamber. These "intermediate" or "reaction" towers have had the greatest success in diminishing the space for the production of sulphuric acid.

One of the first attempts in this direction was the plan of Thyss (G. P. 30,211), of which I have myself given a detailed description in Zsch. f. angew. Ch. 1889, p. 265, abstracted in our second edition, pp. 378 & 379. This system having completely broken down after a short trial, it may suffice to say that Thyss employed lead towers, provided with a number of perforated lead shelves over which the gas had to take a zigzag course. These towers were not fed with any liquid, and consequently they would become very hot and could exert no cooling action; the draught was very much impeded and the lead quickly corroded. Moreover, these towers cost twice as much as a chamber producing the same amount of acid. Still, although the Thyss columns were both an economic and a technical failure, they proved that even in that imperfect form an intimate mixture of the gases and their contact with solid surfaces considerably hasten the reaction.

Much better elaborated was the plan of Sorel (French patent of 1886; comp. his 'Fabrication d'Acide sulfurique,' p. 398, and Zsch. angew. Ch. 1889, p. 279). He proposed to start with a small chamber; from this the gases were to pass through cooling-pipes and then through two or three towers, where steam is also injected, while acid of 142° to 150° Tw. is running down, the out-flowing acid not to fall below 130° Tw. Although he was then connected with one of the largest chemical works in the world, his proposal has never been tried on the large scale, probably owing to constructive difficulties; moreover, his idea of employing *strong* acid for feeding the towers would rob the process of most of the advantages of the principle.

It is recognized on all sides that the object in question was first accomplished by my *"plate-towers"* (Zeitsch. f. angew. Chemie, 1889, p. 385), in which I have endeavoured to combine all the principles hitherto recognized as paramount in the manufacture of sulphuric acid. In the 7th Chapter, when treating of the Theory of the Chamber Process, we shall see that I formulate this theory as follows:—Nitrous acid (or anhydride), or in the first part of the chambers nitric oxide, acts as carrier of atmospheric oxygen and water upon sulphur dioxide, by which action nitrososulphuric acid is formed. This acid, which for the most part at once dissolves in the sulphuric acid already present, like this floats about in the chamber in the shape of a fine mist. When coming into contact with water, or, which is probably the usual case, with dilute sulphuric acid, a decomposition takes place by which sulphuric acid is formed, and all the nitrous acid is returned into the atmosphere of the chamber to recommence the above-described action.

It is evident that all these reactions require in the first instance a most intimate and constantly renewed *mixture* of all the gases, vapours, and misty particles. In the ordinary large chambers a long course, a vast space, and a correspondingly long time are needed till the reactions are practically complete; that is, till nearly all the SO_2 has been removed from the gases. If it were only the question of a mixture of gases and vapours, probably very much less time and space would be required; but as both the nitrososulphuric acid and the dilute sulphuric acid, which are to act upon each other, are in the state of mist, that is, of minute *liquid* drops, they may travel for some distance side by side without coming into actual contact and reacting as they are intended to do. In many similar cases it has been found that simply mixing up the atmosphere in question is nothing like so efficient as presenting large *solid* (or liquid) *surfaces* against which the gaseous current must strike in its progress. By the shock against these surfaces, and the loss of velocity thereby incurred, and undoubtedly also by surface attraction, the misty particles which would otherwise float about for hours in the same state are condensed on those surfaces in larger drops or films, and then the mutual reaction above described, leading to the splitting up of nitrososulphuric acid, will take place at once. From this we infer that we ought to arrange a number of large solid surfaces in the path of the gaseous current, but so arrange them that this current must continually strike against them and be constantly broken up into small parts and mixed up again. (In this respect Ward's glass sheets, p. 473, running parallel with the gaseous current, were not properly disposed.)

There is, however, another condition to be realized for a proper working of the chamber process. As we shall see further on, it is indispensable that the *temperature* of the chamber is kept sufficiently low to condense the requisite quantity of aqueous vapour into liquid water or dilute acid, sufficient for decomposing the nitrososulphuric acid. As the reactions in progress within the chambers produce a large quantity of heat, the process cannot go on without a portion of that heat being abstracted again, which in the ordinary system is done by radiation from the chamber-sides. The separation of the whole chamber-space into several smaller chambers acts favourably in this respect, as the ends of the chambers and the connecting-pipes act as cooling surfaces; and Sorel (comp. above) actually proposed increasing this by arranging a set of cooling-pipes, which, however, would be nothing like sufficient for the purpose. My own plan is, however, different from anything hitherto proposed. I effect the necessary lowering of the temperature, not by radiation or convection to the outer air, but from within by a shower of water or very dilute sulphuric acid. Thus several objects are attained at the same time. The

Fig. 182.

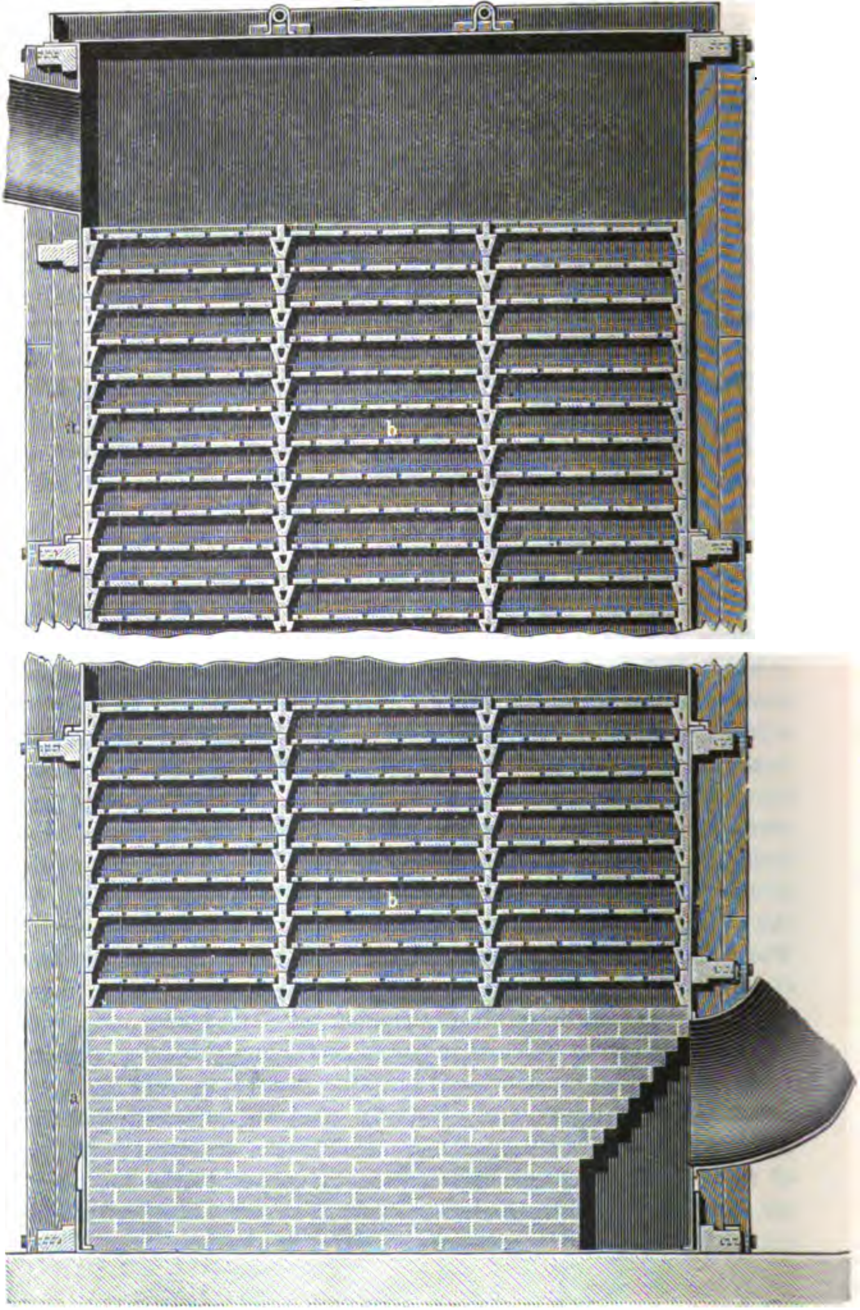


Fig. 183.

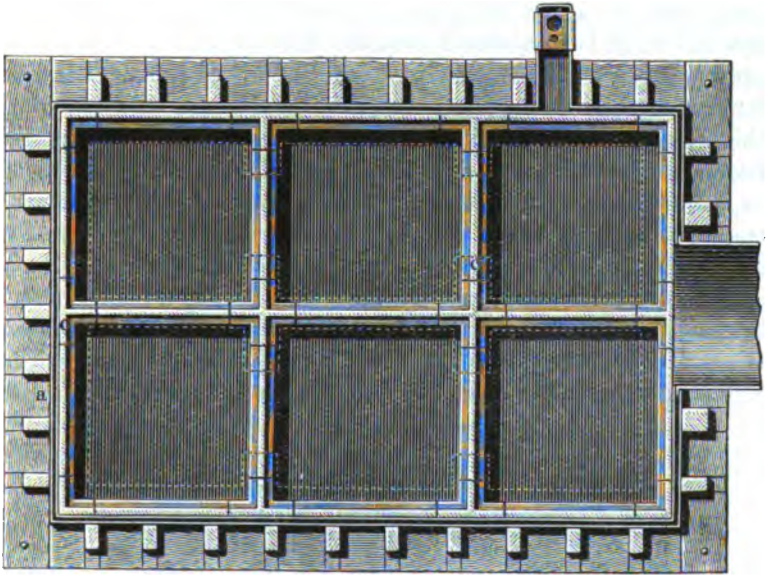
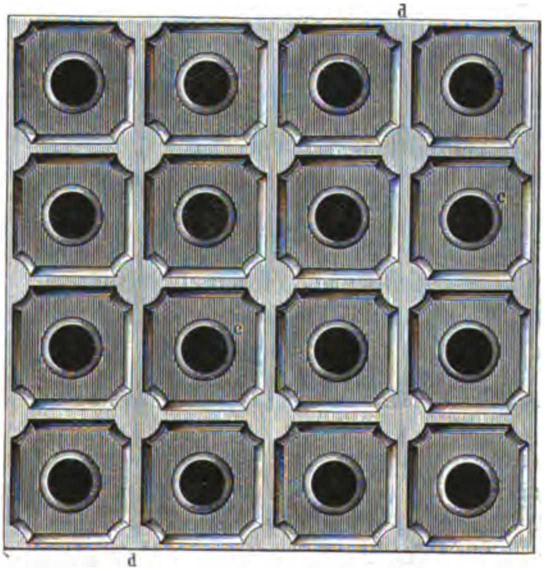


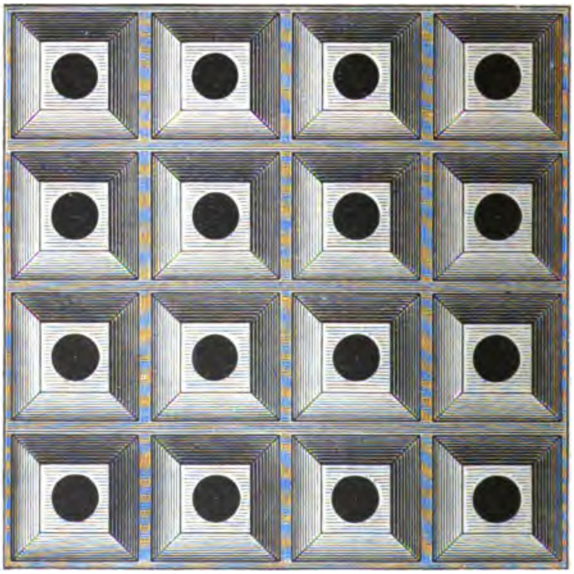
Fig. 184.



temperature of the chamber atmosphere is reduced to a proper level, parts of its heat being spent in heating and vaporizing water; but this water is just what is required for carrying on the chamber process itself, and thus a saving is effected in the raising of steam for the purpose of supplying the vitriol-chambers; we also supply this water in a finely divided form, and exactly where it is needed for meeting and decomposing the nitrososulphuric acid condensing on the solid surfaces; and by this cooling we protect the apparatus employed against rapid deterioration, such as occurred in the Thyss plan (p. 477).

The apparatus employed is the "plate-column" or "plate-tower," invented by myself and patented with Ludwig Rohrmann (E. P. 10,355 of 1886; 10,037, 1887; 6989, 1889). It originally consisted of a column of large stoneware cylinders, filled with the plates forming the peculiarity of the invention; and this is the construction still employed for nitric and hydrochloric acid (p. 125); but for the purpose of sulphuric-acid manufacture it is constructed with a leaden shell (*a*) of either round or angular

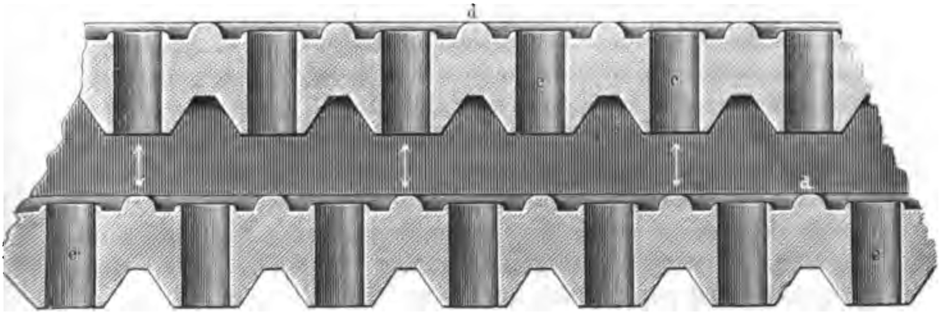
Fig. 185.



section, and stoneware plates (*b b*), as shown in figs. 182 & 183. The plates are supported by bearers, *c c*, in such a way that each plate is independent of the others, and presses only upon the horizontal ledge of its own bearer, whilst the pressure of the superposed plates and bearers is sustained by the vertical part of the bearers. The latter are easily arranged so as to protect the whole inner surface of the lead against the attack of the chemicals and the high temperature ruling within. We do not here notice such parts as the feeding-arrangements, inlet- and outlet-pipes, and the like, which require no special explanation; the feeding-arrangement will be described in the 6th Chapter, in connection with the Gay-Lussac tower. A special explanation is only necessary for the plates *b b*. Fig. 184 shows a small portion of their surface as seen from the top, fig. 185 the same as seen from the bottom, fig. 186 a section of pieces of two superposed plates.

Each of these is covered with a network of small ledges, *d d*, and in each of the squares thus formed there is a perforation, *e e*, with a somewhat raised margin. The height of this margin is not quite so great as that of the ledges, hence there is always a layer of liquid about $\frac{1}{8}$ inch deep in each of the squares; and as there is always more liquid dropping in, the excess is forced out through the perforations drop by drop. The plates are not identical in shape, but differ as to the position of the holes. To each perforation in any one plate there corresponds the point of union of the ledges in the plates above and below (see fig. 186). Hence the liquid cannot drop straight through the holes in the following plates, but strikes the solid portion of the next plate, is

Fig. 186.



scattered about, and is divided among the adjoining squares. This action is repeated from plate to plate. Thus the thin layer of liquid resting upon the plates and clinging to the holes is constantly renewed, and by the scattering about of the liquid another absorbing surface is created.

The gases and vapours rising within the tower pass through the numerous holes of the lowermost plate and are thus divided into a great number of fine jets. Immediately on issuing through the holes of this plate, they strike against the solid places in the next plate above, which correspond to the holes, and are thus divided and again mixed; and this process is repeated as many times as there are plates provided. Whilst the gases and vapours thus travel upwards in continuously renewed mixtures they come into the most intimate contact with the absorbing-liquid, which they meet within the narrow holes on the plates and scattered all over in fine drops. By the incessant changes in the direction of the current, and the equally incessant renewal of the surface of the liquid, the most favourable conditions are produced for a mutual action of the gaseous and liquid substances. Owing to the principle of the apparatus, no false channels can exist in which the gases or liquids would travel separately without coming into proper contact with each other.

This circumstance partly accounts for the enormous difference in condensing-power between the "plate-tower" and a perfectly well-constructed and packed coke-tower, or any similar apparatus, fitted with pieces of pottery and the like. The liquid within a coke-tower is never quite evenly distributed; there are always many places where it drops down a considerable height without meeting a piece of coke, and where, on the other hand, the gases find channels in which they can ascend without for some time getting mixed and coming into contact with liquid. Moreover, the individual gas-channels are too wide, and the inner portion of the gaseous current does not enter into reaction with the absorbing-liquid. This is unavoidable, because the interstices between the pieces of coke are quite irregular, and therefore the section of the tower must be made wide enough and the pieces of coke large enough to secure a sufficiency of draught for the worst case. Nor, as experience has demonstrated, have any arrangements of cylinders, pipes, or other pieces of pottery hitherto had a better effect than coke. Hence coke-towers must be made very wide and high, thus offering a long time and corresponding opportunities for mixing the gases and enabling them to come into contact with the liquid; and in this way the reaction is certainly very complete at the end. But this enormous enlargement of space can be avoided by the systematic way in which, in the plate-tower, the gaseous current is split up into upwards of a thousand very thin and exactly equal jets, which must continually alter their direction, and must therefore become thoroughly mixed each time they pass through a new plate. On their way they come into the most intimate contact with constantly and systematically renewed thin layers of liquid. The network of ledges prevents any unequal downward passage of the liquid, unlike the action of coke-towers or of any other hitherto known form of similar apparatus. Perhaps a still more important difference is the following:—There is a very thin and constantly renewed layer of liquid spread over each plate, and the gases, in passing through the perforations of the plate, must frequently break through the drops of liquid. This seems to produce an action somewhat similar to the Coffey still or other "rectifying" apparatus, and it may to a great extent explain why such an intense action takes place in so small a space.

Owing to these advantages a plate-tower, in comparison with a coke-tower, does from ten to twenty times as much work in the same cubic space. It can therefore be made not merely much smaller in section, but also much lower in height, and the feeding-liquid requires correspondingly less pumping. A column of 40 plates would be only 18 feet high. The above is a comparison between plate-towers and coke-towers; the difference between the former and empty chamber-space is much greater, as we shall see.

In our present case it is of special importance that the injurious action exerted by the reducing power of coke upon the nitrous gases (p. 231) is avoided, the stoneware plates being absolutely stable in the chamber atmosphere if manufactured of proper quality. The plates, therefore, last for ever; even if cracked they may still continue in use.

When a plate-column is partly obstructed by muddy deposits, it is very easily cleaned out by a thorough flushing with water, or, in bad cases, by removing the cover and lifting out one plate after another.

Apart from the great constructive difference between the plate-towers and all previously proposed apparatus, there is an equally great difference in their mode of application. If the tower were left to itself, like Ward's or Thyss's apparatus, the very completeness of the mixture produced therein would produce an intense chemical reaction, and, consequently, a very injurious development of heat. This is, however, entirely avoided by feeding the towers with a stream of water or dilute sulphuric acid, at such a rate that, by the vaporization of water, the temperature does not rise above 70° or 80°. The intimate contact between gaseous and liquid particles within the plate-tower must bring out the cooling action of the evaporation of water to its fullest extent, and at the same time the water required for the chemical reactions of the acid-making process is supplied here without any previous production of steam or spray; the superfluous steam passes over into the next chamber and does its work there. The acid running off at the bottom is either used up as it is, or is run into one of the chambers, or it is employed for feeding the Gay-Lussac tower.

In plate-towers there will always be a great excess of nitrous gas and of oxygen; hence there is very little fear that even when employing water for feeding them there will be the conditions present for the formation of nitrous oxide, which would mean a waste of nitre. This can be avoided in any case by feeding the columns with sulphuric acid of 1·3 spec. grav. or upwards, since I have already shown (Ber. d. deutsch. chem. Ges. 1881, p. 2200; comp. *supra*, p. 218) that in this case no N_2O whatever is formed. In practice such dilute acid or chamber-acid is employed for feeding the columns.

The principal advantage of this system is that, like the Glover tower, it brings about the mutual action of the ingredients within the smallest possible space. We shall see in Chapter VI. that one cubic foot space in the Glover tower effects the formation of as much acid as at least 180 cubic feet of ordinary chamber-space; and a similar difference may be looked for between the latter and the plate-towers to be interposed between the chambers.

We will now consider the question whether the thermal effects produced in that system are not excessively large or small. The heat of forming H_2SO_4 from SO_2+O+H_2O is 54,400 calories; to this must be added the heat produced in the formation of ordinary chamber-acid, say, of 110° Twaddell, or H_2SO_4, 3 H_2O

=11,100 calories; altogether 65,500 calories. This is the heat produced in the formation of a quantity of chamber-acid corresponding to 98 grams of H_2SO_4, and it is very little more than would be required for converting 98 grams of cold water into steam. This quantity of water then would have to be evaporated within the tower in order to absorb all the heat produced in the acid-forming process, on condition that the acid must run out cold at the bottom and that the tower would lose no heat by radiation. But as the former condition is unnecessary, and the latter even impossible to maintain, the quantity of water evaporated will be less than the weight of monohydrate produced, and will probably be very nearly equal to that required for the chamber-process, viz. three quarters of that amount. Any deficiency of water could, of course, be made up by steam, probably best by means of an injector placed in the outlet tube from the plate-tower.

As a practical way of applying the new system, I proposed from the first the following plan :—Considering that by far the greatest portion of the acid is made in the first part of the chamber, we cut off the back part altogether, and leave behind the Glover tower a chamber of only about 50 feet length. Behind this we place a plate-tower of sufficient section for the amount of gas to pass through and 40 plates high (say 18 feet). Then comes a small chamber, say 30 feet long, again a plate-tower, a last chamber for drying the gases, and in the end a plate-tower serving as Gay-Lussac tower.

The question might be raised why I did not propose to carry on the whole of the sulphuric-acid-making process in plate-towers or similar apparatus. But a glance at the curves shown in the 7th Chapter will show that the first part of the first chamber is really very efficient, and whilst the gases are of such concentration a lead chamber is possibly the cheapest apparatus for making sulphuric acid. As soon as the curves begin to bend towards the horizontal, that is, when the reactions become sluggish, it is time to liven them up by apparatus like the plate-towers. But if such were attempted to be used from the first, the heat would become excessive, which would be very injurious both to the material of the apparatus and to the process. For this reason the process proposed by Hannay (E. P. 12,247, of 1886, comp. Chap. XII.) is not likely to be practically successful.

The first factory which ventured to try my plate-towers (which have become known as "Lunge towers," both in their application as intermediate "reaction" towers for the vitriol-chambers, and as replacing coke-towers for the recovery of nitrogen acids, for condensing hydrochloric acid, and so forth) was the old-established acid-works at Lukawetz, in Bohemia, soon followed by a factory at Valencia, in Spain, both in 1891, and by others in various countries. Of course here and there difficulties were experienced, principally caused by the obstruction of draught. Thus in Zsch. f. angew. Ch. 1895, p. 407, P. W. Hofmann alluded to a trial which failed because the holes in the plates, 8 millm. bore, became filled with liquid and thus stopped the draught. I myself (ibid. p. 409) completely refuted this objection, mentioning that already about 200 plate-towers were then at work, most of them with even smaller holes, and a large number with 8 millim. holes, in sulphuric-acid works. These works had been very successful, as was authentically proved by the replies to interrogations put to certain firms, which also show that, if the section of the tower is sufficiently large, no trouble is caused by draught of the kind mentioned by Hofmann. Since the principle of artificial draught by means of fan-blasts is becoming more and more applied to vitriol-chambers, the complaint against the plate-towers on the above ground is practically meaningless.

The greatest development of the plate-tower system took place when H. H. Niedenführ, chemical engineer of Berlin, took the matter in hand. He has designed and started many chamber-plants on that system, and studied all the conditions necessary for success, so that I shall refer principally to him in the following description.

The part played by the Lunge towers in the manufacture of sulphuric acid has been discussed at length by Niedenführ, in 'Chem. Zeit.' 1896, p. 31. According to him, plate-towers are not very well adapted for replacing the whole of the ordinary vitriol-chambers ; the first part of the process is always best carried out in a single lead chamber, as here the gases are still sufficiently concentrated to react upon each other. [In this view, as well as in all other essential points of Niedenführ's paper, I fully concur.] Here also the flue-dust and the excessive rise of temperature would act injuriously. Hence it is not advantageous to place a Lunge tower between the Glover tower and the first chamber, but it should be placed in the central or back part of the set of chambers. Even then the results obtained with these towers do and must differ at different works, according to circumstances, viz., the available chamber-space, the draught, the size of the burners and of the connecting-pipes, of the Gay-Lussac tower, and so forth. In some cases the working capacity of the tower is partly taken up for correcting some fault in the set of chambers to which it has been applied. Niedenführ quotes the following special instances of the work done by Lunge towers, as personally observed by him in the cases stated.

In one case, a Lunge tower was placed between the two chambers of a set, which were of equal size; the total length of the set was 193 ft. 6 in. and its contents = 94,640 cubic feet. The quantity of Sicilian sulphur burnt previously did not exceed 30 cwt. per 24 hours; but after putting up the tower it could be raised to 46 cwt., evidently because the time and the length of the path of the gases had been thereby increased to such an extent that the set could be worked with stronger draught, and more sulphur could be burnt accordingly. In another case (4 chambers, total capacity 38,150 cubic feet, length 78 ft. 6 in.) the production could be increased from 15 to 18 cwt. of Sicilian sulphur per day. This means that some improvement had been effected, but principally in this respect, that the previously observed fault, viz. the carrying forward of the process into the Gay-Lussac, was now avoided. In a similar case, the production rose from 16 to 19 cwt. of sulphur; in both cases less nitre was consumed than previously. The towers thus spent part of their efficiency in correcting the faults of the old plant, and this in many cases would be a very desirable object; but the quantitative results thus obtained do not represent the whole of the working capacity of the towers, which in some more favourable cases has admitted of increasing the production by 45 per cent. Nearly in every case observed by Niedenführ this capacity of the towers had not been exhausted, for the chamber following upon the towers had hardly any more work to do; more work could have been done by increasing the number of the burners, by enlarging the connecting-pipes, or by other suitable measures. The very low temperature of the back chambers in this case, however, is useful in condensing part of the nitrous gases and lightening the work of the Gay-Lussac tower. Formerly the acid from the Lunge towers was sometimes too nitrous, but this drawback has been avoided by feeding the towers with acid of from 38° to 42° Bé. (spec. grav. 1·357 to 1·410).

The Lunge tower cannot be simply substituted for a Glover tower, as the holes of the plates would be too quickly stopped up by flue-dust, and in washing this down they would easily crack. Niedenführ, however, recommends placing a few tiers of plates with ½-inch holes in the upper part of the tower. He quotes a case where a Lunge tower was found specially useful in completely denitrating chamber-acid required to be entirely free from nitrogen compounds. [Comp. another case of special utility in the 6th Chapter.]

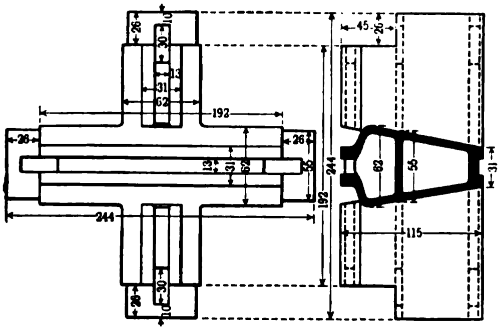
Especially good results have been obtained in a number of cases, personally observed by Niedenführ, where plate-towers were employed as auxiliaries to Gay-Lussac towers. They act not merely in promoting the absorption of the nitrous gases, but also in rendering the chamber-work much more regular, especially in places where the chambers are subjected to sudden changes of weather, gales, &c.

Niedenführ in the above-quoted paper makes certain proposals for the erection of sulphuric-acid works, forming a combination of chambers and plate-towers, which we do not quote here, because they are rendered obsolete by recent experience, the result of which will be noticed in the 10th Chapter, where a complete plan for this purpose will be given. [Comp. also p. 496.]

Lüty (Zsch. angew. Ch. 1897, p. 484) also discusses at length the function of "Lunge towers" as intermediate reaction-towers. He quotes the results of ten different works employing such towers between the chambers as means for reducing the chamber-space, from England, Scotland, Spain, Russia, Denmark, showing a large saving of space, without any increase in the consumption of nitre. He also gives detailed estimates showing that, apart from the saving of ground-space, a set of chambers provided with such reaction-towers costs 35 per cent. less than ordinary chambers for the same production.

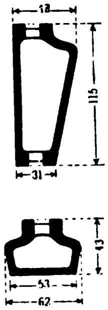
More recently, Niedenführ (Chem. Zeit. 1897, no. 20) quotes practical results from two English works. One of them replaced the last chamber of a set, with a capacity of 38,390 cub. feet, by a Lunge tower of 256 plates in 16 layers, with the same make as before. Here each plate actually made 10·6 kils. H_2SO_4 in

Fig. 188.



Scale 1:6

Fig. 189.



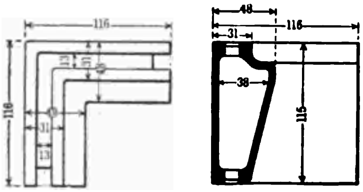


Fig. 187.

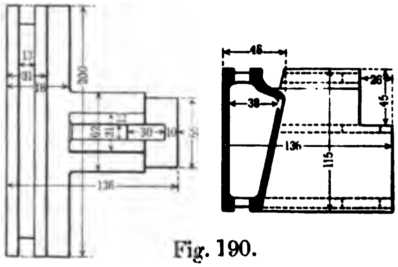


Fig. 190.

Fig. 191.

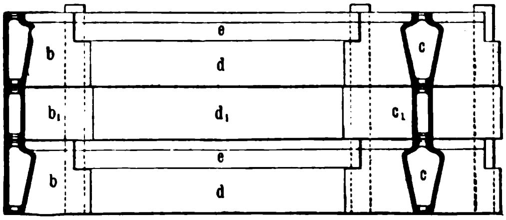
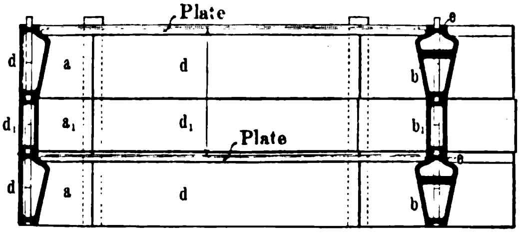


Fig. 192.



Scale 1:12

24 hours, or 216·7 kils. per cubic metre of the space filled with plates, *e. g.* about 100 times as much as ordinary lead chambers. Another factory, with very poor gases, still made 88·3 kils. H_2SO_4 per cubic metre of plate-space. [Comp. also Zsch. angew. Ch. 1900, p. 960.]

Niedenführ (private communication) gives the following detailed instructions for the erection of Lunge towers, taking, for instance, a tower of a sectional area of 20 plates, 2 feet square each, placed 4 × 5.

A brick foundation is usually made, but in case of need the tower can be placed on the flooring surrounding the chambers, if properly supported. The leaden shell is erected, with its outer frame of wood and a lead bottom. On this a dwarf wall of 9-inch fire-bricks is placed all round the circumference, and a central supporting pillar. This wall supports an iron frame, consisting of one or more (in this case of six) pieces. The middle pillar supports the places where four of the six pieces meet. This frame is covered with lead, the joints being so arranged that the upper, bearing surface remains free and smooth. On this frame the stoneware bearers (figs. 187–192) are placed. There are corner pieces, *a*, which carry one of the corners of the plates, the three others being supported by T-pieces *b* and cross-pieces *c*. Between these pieces the longitudinal bearers are placed along the lead sides of the tower. In order to prevent any shifting of the pieces, wedges are put in suitable places.

Upon the frames thus prepared the Lunge plates are put, and after finishing off one layer the parts forming the next frame are placed upon the corresponding cross- and angle-pieces &c. The parts *a, b, c* are so chosen that there is a distance of 2½ inches between the single layers of plates. If a greater distance is desired, we place below the parts *a, b, c* other cross-, T-, and angle-pieces, a_1, b_1, c_1, 3·14 inches high. According to the number of layers of bearing-pieces we designate the distance from plate to plate as single, double, treble, &c. The tower in question has in its lower part 10 layers at single distances and 6 layers with double distances.

The top of the tower is made of lead, and is provided with a proper feeding-arrangement.

If plate-towers are to be combined with existing systems, it is of course necessary to consider the place and level where the towers are to be erected, and their dimensions, in connection with the existing circumstances, so that it is difficult to lay down general rules. But where new plant is to be erected, long experience now admits of establishing certain rules.

It is possible (as Mr. Niedenführ now holds) to replace the lead chambers altogether by Lunge towers, by taking care to erect the first part with as little loss of draught as possible, and to remove the heat of reaction to the necessary extent. This is done by making the reaction towers, immediately following the Glover towers, of a wider section, and providing them with a very efficient feeding arrangement. The last towers must be made narrower than corresponds to the volume of gases passing through the first towers, so as to exert a certain pressure on the gases which promotes the reaction. The plate distances in these final towers must be kept smaller than in the first towers.

The horizontal sections of Lunge towers may be chosen according to the following particulars :—

Sulphur to be burnt per 24 hours.	Number of plates to be employed per ton of sulphur burnt in 24 hours to replace the chambers in different parts of the system:—		
	in front.	in the middle.	in the rear.
Up to 1 ton S	12	10	6
From 1 to 2½ tons S......	12 to 10	10 to 8	6 to 5
From 2½ to 5 tons S......	10 to 6	8 to 5	5 to 4

The number of layers for a given production is calculated as follows :—In the first third of a system, where the plates are at a treble distance from each other, each plate may be assumed to produce in 24 hours from 10 to 12 kils. H_2SO_4; in the second third, with double distances, each plate = 6 to 8 kils. H_2SO_4, in the last third, with single distances, 1·25 to 2 kils. H_2SO_4.

Just as it is irrational to make a chamber system of one chamber only, which favours the diffusion of the inactive residual gases with the active ones, it would be wrong to try manufacturing with one tower only, instead of dividing the work over several towers.

Mr. Niedenführ believes the following arrangement to be suitable for working with towers alone, without chambers (figs. 193 and 194). The burner-gases pass through *a* into a preliminary tower *b*, and through *c* into the fan-blast *d*, which conveys them through *e* to the denitrator *f*. This apparatus is fed with nitrous vitriol and warm water or dilute acid so as to furnish acid of 54° B. (=119½° Tw.). It also receives the nitric acid required for making up the losses. It is packed like a Glover tower, preferably with dish-like packing. Part of the acid here made is employed for feeding tower *b*. This denitrating tower is constructed on the same principle as Niedenführ's ordinary Glover towers (comp. next Chapter), viz. with an interruption of the packing intended to facilitate the cleaning of the bottom part, and with sufficiently large openings for the passage of the gas. In tower *b* the acid with which it is fed is concentrated, the gases are purified and partly cooled so that they may pass through the fan-blast without any trouble. They effect the denitration in *f* and then pass through g_1, g_2, to the first plate-tower *h*; pipes g_1, g_2, as well as the further pipes i_1, i_2, are provided with steam-pipes. Tower *h* is filled with 12 layers of 24 plates each in treble

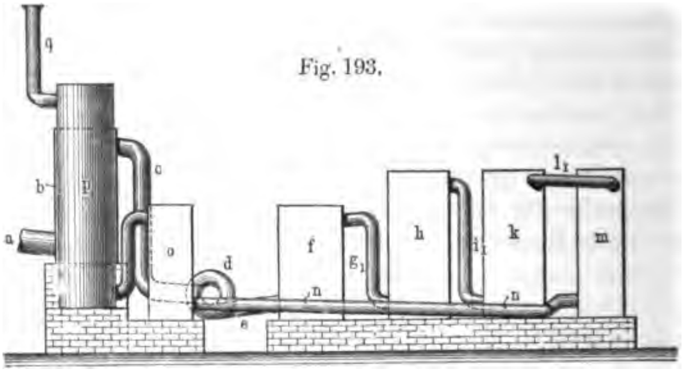


Fig. 193.

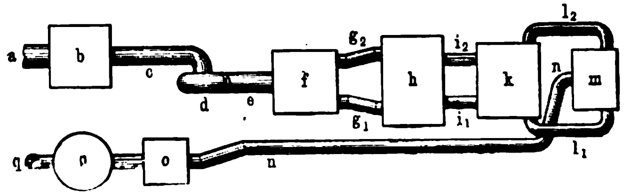


Fig. 194.

distances; tower *k* with 18 layers of 20 plates each in double distances. In *h* and *k* the gases enter at the bottom and issue at the top; but in the last reaction-tower *m* they enter at the top and leave it at the bottom through *n*, which arrangement has been found to give the best result. Tower *m* contains 30 layers of 12 plates each in single distances. The gases now pass into the first Gay-Lussac tower *o*, containing 16 layers of 9 plates each, then into the second Gay-Lussac *p*, packed with coke, and finally through *q* into the open air.

Fig. 195.

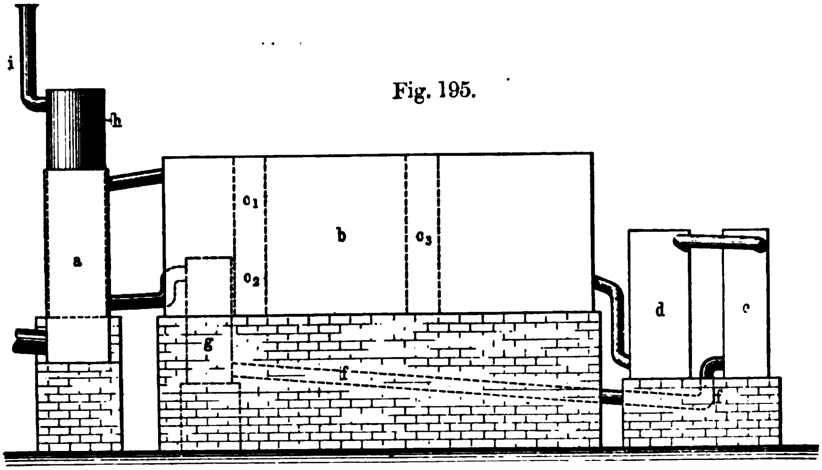
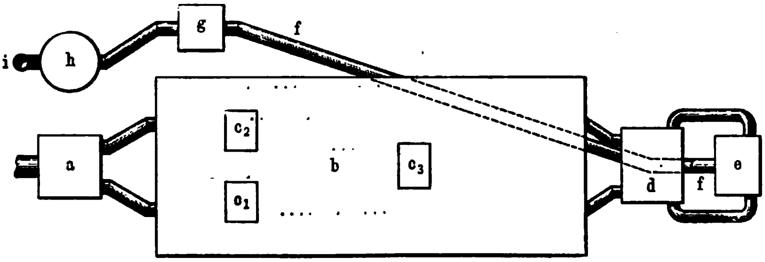


Fig. 196.



The acid coming from the first Glover tower *b* is freed from most of its impurities by means of an air-cooler.

The just described system would serve to treat the gases from

2500 kils. = 2½ tons sulphur per diem. The production of acid would be divided as follows:—

Tower *h*, 288 plates at 10 kils. H_2SO_4 = 3168 kils. H_2SO_4.
„ *k*, 360 „ „ 7 „ „ = 2520 „ „
„ *m*, 360 „ „ 1·75 „ „ = 630 „ „
Glover and Gay-Lussac towers............. 882 „ „

Total ......7200 „ „

If the same production is to be attained by means of a combination of chambers and plate-towers, this can be done as shown in figs. 195 & 196.

From the Glover tower, *a*, the gases pass into a lead chamber, *b*, containing 1064 cub. metres = about 38,000 cub. feet, provided with air-cooling shafts, c_1, c_2, c_3 (comp. p. 477). In this case no fan-blast need be employed, but the gases must have a sufficient upward draught from the burners to the Glover tower and from this to the chamber *b*. Now come the two plate-towers *d* and *e*. These, as well as tower *a*, may be placed at a lower level, which is all the better for the work. The Lunge tower *d* receives 20 layers of 20 plates each in double distances, tower *e* 30 layers of 12 plates each in single distances. At *e* the gases are passed in at the bottom and out at the top, and then through *f* into the first Gay-Lussac tower (a plate-tower) *g*, into the coke-packed Gay-Lussac *h*, and through *i* into the open air. The production will be approximately divided as follows:—

Chamber *b*, 1054 cub. met. at 2·75 kils. = 2926 kils. H_2SO_4.
Tower *d*, 400 plates at 7 kils. .... 2800 „ „
„ *e*, 360 plates at 1·75 kils............. 630 „ „
Glover and Gay-Lussac towers .... 844 „ „

Total 7200

In a similar way larger systems can be constructed with one chamber and a suitable number of Lunge towers. Mr. Niedenführ would not even for the largest systems propose more than two chambers, placing between them a very wide plate-tower with great distances, and behind the second chamber all the remaining towers. In the 10th Chapter complete plans will be given for such a combination.

In order to apply the Lunge towers to existing systems, for the purpose of increasing the production, the circumstances of each case must be critically considered in the light of the large experience now gained. It will usually be best to place the towers behind the last chamber. The horizontal section of the towers can be calculated from the last column of the table given on p. 493; in the case of very large systems from the second and the last column; with good draught the plates should be kept at single or double distances.

If, however, plate-towers are to be placed *between* existing chambers, all the conditions of the system must be carefully considered according to the experience gained therewith. Above all, the towers in large systems should not be arranged just after the front chamber, but between the back chambers. The horizontal sections, the places in the system, &c. must be calculated according to the general instructions given above. If we were, for instance, to place a Lunge tower between No. I. and No. II. in a system of four chambers, the last three chambers would do very little work. It will be much better to place the tower between Nos. III. and IV. or behind No. IV.

Mr. Niedenführ thinks that, in view of the considerable saving of expense effected by these improvements of the ordinary chamber process, the contact systems cannot compete with the former in the production of acid up to 142° Tw., and show their superiority only for acids above that strength.

A very instructive plant was erected by Mr. Niedenführ at the "Lazyhütte" works. The chamber system consisted originally of four chambers, with a total capacity of 7110 cub. met. (=250,000 cub. feet), and three Glover towers, two of which were always working at the same time. In 1900, working with zinc-blende and "forced style," this set produced on an average 25,580 kils. acid of 50° B. (106° Tw.) per 24 hours, with 3·03 nitric acid 36° B. per cent. sulphuric acid. In 1901 four Lunge towers were erected behind the last chamber, viz.: No. I. 12 layers at 20 plates, double distances; No. II. 16 layers at 20 plates, partly single, partly double distances; No. III. 25 layers at 16 plates, single distances; No. IV. (acting as a first Gay-Lussac tower) 18 layers at 25 plates, single distances. The production now rose to 36,450 kils. acid of 50° B., with 1·90 per cent. nitric acid 36° B. per cent. sulphuric acid. Evidently the plant was not working up to its full capacity, but as there was not enough draught, a fan-blast was placed behind tower No. IV. The production of acid rose at once, but during a few days also the consumption of nitric acid (to 4·76 acid 36° B. per cent.). When, by a number of tests, the draught had been properly regulated (which is still not quite perfect, since there is only a temporary source of power for the fan-blast, to be replaced by a better engine at the first opportunity), the production rose permanently to 44,600 kils. acid of 50° B., with a consumption of only 1·7 per cent. nitric acid 36° B. This, for Upper Silesian zinc-ores, is a most excellent result, both as to production of acid and saving of nitre.

The following estimations of temperature and manometric pressure, made with this system, after the erection of the plate-towers, at three specified times (viz., before and after the increase of draught by means of the fan-blast), are quoted here for the sake of indicating their connection with the above-mentioned alterations, but we shall later on describe the regulation of temperature and draught of chamber systems.

Place where the observations were made.	Before applying the fan-blast (Sept. and Oct.).		After applying the fan-blast (November and December).			
			Before properly regulating the draught.		After thoroughly regulating the draught.	
	Pressure mm. water.	°C.	Pressure mm. water.	°C.	pressure mm. water.	C.
Gas-pipe between Ch. I. & II	+1·6	90	+1·0	104	+1·9	91
„ „ Ch. II. & III.	+1·1	69	+0·2	86	+0·5	73·5
„ „ Ch. III. & IV.	+0·75	54	−1·0	...	−0·5	60
„ „ Ch. IV. & Tower I.	+0·6	...	−3·8	...	−4·3	...
„ „ Tower I. & II.......	−0·9	...	−5·0	...	−5·8	...
„ „ „ II. & III....	−1·6	...	−6·2	...	−7·1	...
„ „ „ III. & Gay-Lussac (IV.).	−3·6	38	+7·4	...	+7·4	30
„ „ „ IV. & Coke-tower (Gay-Lussac).	−4·5	...	+4·8	...	+4·0	...
„ „ Coke Gay-Lussac & chimney	−9·4	...	−1·4	...	−5·0	...

Other Apparatus on the principle of Plate-towers.—After the success of the principle embodied in the "plate-towers" had been thoroughly established, it was only natural that other inventors should try, more or less successfully, to attain the same end by other means, not coming under the Lunge-Rohrmann patents. This was all the more likely, as the price of the "plates" and the fittings belonging to them was at first rather high, owing to the technical difficulties of their manufacture. Since these difficulties have been entirely overcome, the price of the plates &c. has been so very much reduced that most of the imitations have lost even any economical advantage, apart from their inferior efficiency. I shall, however, quote all the more important of these imitations.

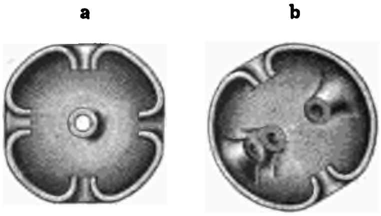
One of the objects aimed at by some of the inventions concerned is to avoid any impediment to the draught, for which the plate-towers are sometimes blamed. As we have seen (p. 498), this objection is of no account in view of the ease with which the chamber-draught can be regulated by fan-blasts, and it should be borne in mind that the efficiency of an apparatus of this kind is practically proportionate precisely to its draught-impeding capacity.

Hacker and Gilchrist (Engl. patent 15,895, 1893) employ the same principle that I have adopted in the "plate-towers," to which they expressly refer. Instead of my geometrically constructed stoneware plates for dividing the gases, the liquid acid, and the acid vapour, they use a number of horizontal lead tubes, running from one side of the tower to the other and alternating in position. These towers, which they call "pipe-towers," are fed with water or sulphuric acid; cold air is drawn or blown through the pipes. A paper in Journ. Soc. Chem. Ind. 1894, p. 1142, contains a detailed account of this system, in discussing which several speakers threw great doubt upon its efficiency. This is hardly just, as the introduction of these "pipe-towers" into many American factories seems to show. They cannot possibly do as much work as "plate-columns" of the same size, but undoubtedly they are of some use. Another paper on these towers was published in Journ. Soc. Chem. Ind. 1899, p. 461, containing some improvements in details. The success of this system as intermediate towers between the chambers is the best proof of the correctness of the principles which led me to the construction and application of the "plate-columns," of which the "pipe-towers" are an imperfect imitation, made of a material liable to corrosion instead of indestructible stoneware. A similar plan is that of Winsloe & Hart (B. P. 20,142, of 1901), who employ perpendicular air-cooling pipes in a shaft connecting two chambers.

Benker (French pat. 238,872) places between the chambers leaden towers, 5 feet wide and 20 or 25 feet high, filled with earthenware cylinders 4 inches wide and 3 to 4 inches high. These are fed with nitrous vitriol from the Gay-Lussac towers at the top, and with a steam-jet at the bottom. The strength of the outflowing acid is maintained between 112° and 123° Tw.; it is kept a little nitrous, to avoid the reduction going too far. Such a tower is placed behind the first chamber, which is made large enough to consume all the steam coming from the Glover tower; another tower is placed between the second and third chambers.—This is, of course, a simple imitation of Lunge towers by cheap, but imperfect means.

Guttmann (G.P.91,815) recommends as a "packing" for reaction-towers perforated globular bodies made of earthenware, glass, or metal. As shown in fig. 197, the perforations are continued into short pipes turning into the inside of the globe.

Fig. 197.



These bodies may also be undulated inside and outside, to increase the acting surface. They can be put into the tower without any special care in packing. The liquid runs down both inside and outside, and the gases are well mixed.

Niedenführ objects to hollow balls on the system of Guttmann and others, because, firstly, most of the perforations get closed up when filling the tower; secondly, the gases are sure to take the easier way round the balls, instead of forcing their way with increased friction into the interior, and whatever does enter the balls will remain there for an indefinite time without taking part in the reactions.

Another kind of reaction-apparatus consists of the "Kegelthürme" (cone-towers) of the Bettenhausen ceramic works. They are filled with slightly conical bodies, open at the bottom and provided with a shallow basin at the top. Niedenführ (Chem. Zeit. 1897, No. 20) says that they are much less active in dividing the gas than Lunge plates (only from 14 to 138 times per square metre, against 2400 times in the case of Lunge plates), that they contain less than half the acid-covered surface, and that the hollow space is altogether a mistake, since the gases will stagnate in them. Lüty (*eod. loc.*) also criticizes the Bettenhausen cones adversely. We shall refer to them again in the next and also in the 12th Chapter.

The final result of reducing the chamber-space would be *the complete abolition of lead chambers in the ordinary sense.* On principle, such a step cannot be regarded as irrational or impossible, and it has several times been proposed or attempted, both in former times (comp. p. 476) and recently (comp. p. 493), since the success of the plate-towers had again shown that the vast space of ordinary vitriol-chambers is not indispensable for carrying on the process. We shall discuss some of these proposals in Chap. XII.; here I will only refer to what I have said on p. 487, viz., that for the commencement of the process (that is, behind the Glover tower) I still hold an ordinary, comparatively small, lead chamber to be the cheapest kind of apparatus for the purpose, followed by a number of reaction-towers, *perhaps* alternating with one or two small lead chambers; but the last word has not yet been said in that direction, and it may be that the ordinary lead chambers can be entirely substituted by reaction-towers, although hitherto this has not been economically accomplished, as will be seen in Chap. XII.

Chamber-fittings.

Every set of chambers must contain a number of auxiliary apparatus, which in part are absolutely necessary for the process, and in part serve to check it chemically and technically: the former are essentially those for introducing the nitre, the steam, and the air; the latter, smaller apparatus will be described first.

Drawing-off the acid is never done by cocks attached to the chambers. Such taps might be made of hard lead (4 to 5 Pb to 1 Sb); but they would soon get stopped up with sulphate of lead, and could not very easily be repaired when leaking. It is best to place beside a chamber a round or square lead box, open at the top, of the same height as the upstand of the chamber-bottom, and connected at or near the bottom by a wide pipe with the chamber; or a suitable piece may be burnt on to the chamber, as shown in fig. 198, and the connection made by a slit. The box may be provided with a stopcock; but more usually, as shown in the figure, it carries in its bottom a valve-seat *a* of regulus metal, into which fits a conical plug *b* of the same metal provided with an iron handle covered with lead. The running-off pipe *d* is either burnt to the valve-seat or joined to it by an open funnel; the latter permits the running-off to be more easily observed, but is apt to occasion running over, by getting stopped up. Or, as shown in fig. 199, a lead *siphon* may be employed, with a cup attached at each end, *a a*, which keep it always filled, so that it begins to act as soon as one of its limbs has been put into the acid. The second limb then enters into a large funnel of the running-off pipe *b*.

Fig. 198.

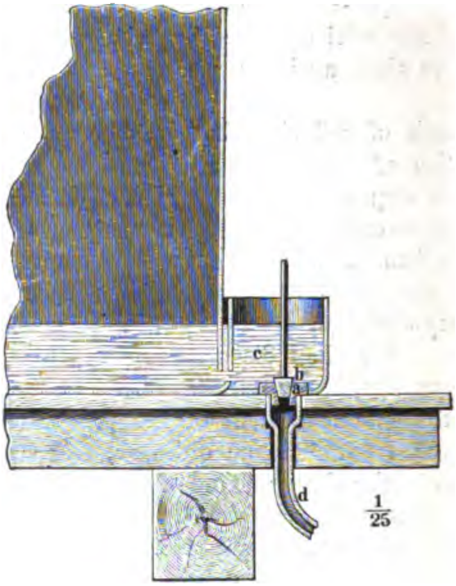
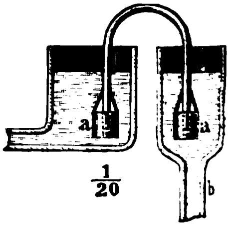


Fig. 199.



The simplest plan, which does not work at all badly, is this: to burn a short piece of thick lead pipe to the chamber-side, and make the joint very strong by casting lead round it. This pipe ends over the funnel of the running-off pipe, and is closed by a good india-rubber cork. The men take this out and put it in by hand, having a bucket of water standing by to wash the acid off their hands.

The arrangement shown in fig. 200 is very good indeed. The siphon *b* is firmly attached to the box *c*, or within the upstand of the chamber. A cylinder *d*, surrounding the outer limb of the siphon, is so suspended that it can be drawn up or down by means of the chain *e* and the pulley *f*, and fixed in any position by the hook *g*. The cylinder *d* forms a continuation of the outer limb of *b*; when it is quite drawn up, so that its overflow *h* is at a higher level than the acid in *c*, it will cease to run; but when *h* gets below this level, the siphon will at once begin to act, and the more quickly the more *d* is lowered. Thus the acid can be run off with more or less speed and with the utmost cleanliness.

Fig. 200.

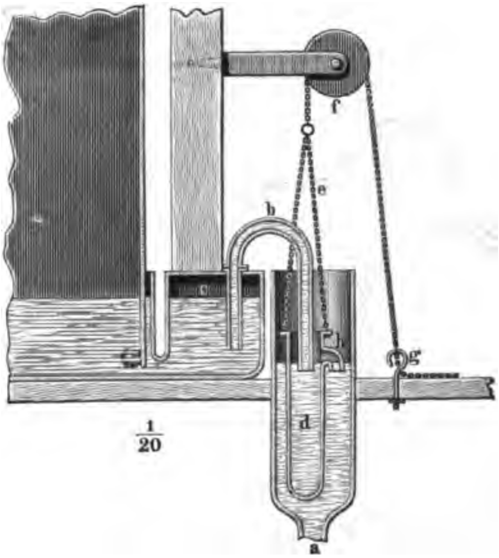
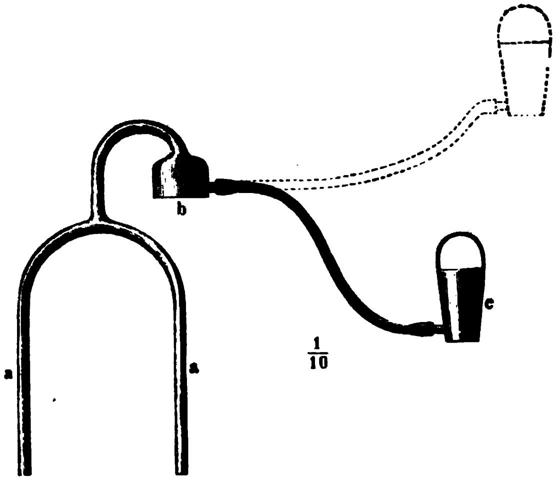


Fig. 201 represents a siphon suitable for hot acids in any part of the works. To the top of the siphon *a a* there is joined by a bent tube a closed lead vessel *b*, which by an elastic tube is connected with the open vessel *c*. The latter is filled with acid and lifted into the dotted position, whereupon *b* and then the siphon *a* are filled; *c* is then lowered, upon which the siphon begins to act, some acid running back from *b* to *c* and thus producing a partial vacuum.

We shall in this place also mention the best arrangements for *inserting siphons into glass carboys* or other vessels for carrying corrosive liquids. The simplest and most efficient plan is that shown in fig. 202. A glass or lead siphon, *a*, is inserted into a good india-rubber cork, made strongly conical so as to fit bottles with various sized necks; another short tube, *b*, passes through the same cork. The siphon, *a*, may or may not be provided with a tap, *c*. It will be seen without explanation that the siphon can be started by blowing into *b*. The flow of liquid may be stopped either by closing the tap *c*, or, if there is no tap, by lifting out the cork, or by opening a third hole provided in the cork for this purpose. In the (very frequent) case of the mouth of the carboys being too irregular in shape for the cork to fit air-tight, the remaining air-channels are stopped up with damp clay; and in an emergency a lump of damp clay may replace the india-rubber cork entirely.

Fig. 201.



Bode and Wimpf's siphon (G. P. 23,794; Chem. Zeit. 1885, p. 907; J. Soc. Chem. Ind. 1885, p. 484; further improvements in Zeitsch. f. angew. Ch. 1889, p. 522) rests on a very similar principle, with addition of a ball-valve for stopping and starting the siphon. It seems to be specially adapted for nitric acid.

Fig. 202.

Fig. 203.

Alisch (G. P. 9133), Landel (G. P. 9307), J. P. y More (G. P. 28,721), Opländer (G. P. 30,662), and others have constructed different kinds of siphons.

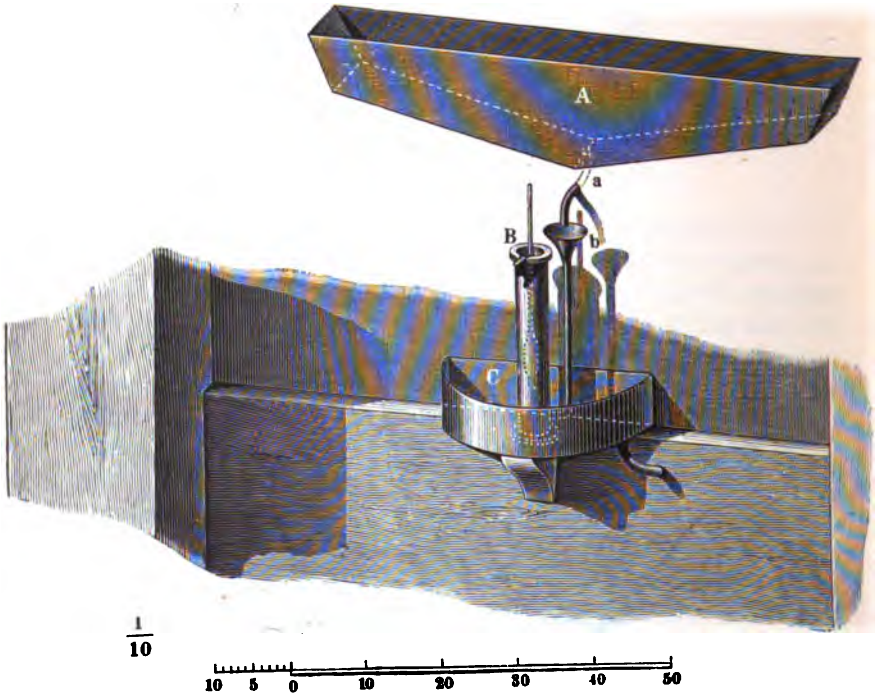
De Hemptinne has written a pamphlet in which he traces a great many forms of siphons to their authors; but there is nothing specially new in it.

Pratt's carboy-emptier, sold by J. J. Griffin & Sons, London, is shown in fig. 203.

J. Cortin, of Newcastle-upon-Tyne, makes ***non-rotative acid valves*** of a special mixture of regulus metal, the plug rising or falling into its seat out of a mixed setting without turning round, so that it is free from friction in working, and the wear and tear are reduced to a minimum.

Acid-dishes (***drips, tell-tales***) are placed inside the chambers, in order to examine the process by ascertaining the quantity, strength, and nitrosity of the condensing acid. They are made in very different ways—for instance, that shown in fig. 204. A is a lead

Fig. 204.



vessel, burnt inside against the chamber-side about 3 feet above the bottom. The acid caught here runs by the tube *a* through the chamber-side into the lead cylinder B, containing a hydrometer. B is provided near its bottom with a side-branch, *b*, reaching above its top, and ending in a funnel for receiving the acid, which thus constantly runs in at the bottom and out at the top of B into a vessel C, from which it is carried back by a small pipe into the chamber. The greater the length of A, the quicker the acid will be renewed in B, and the more reliable are the indications.

Many manufacturers place S-shaped drip-tubes in the connection between the chambers, for a similar purpose. Others do not trust to the collectors burnt to the chamber-sides, but place leaden or stoneware dishes at some distance from the side within the chamber. These rest on feet made of lead tubes, or upon a stand of stoneware, so as to be elevated above the level of the acid; and they have an outlet leading outside the chamber. In some works, both kinds of drips are fixed side by side; and it is noticed that those fixed to the sides always yield acid of 6° to 10° Twaddell less than the inner drips, evidently because more aqueous vapour is condensed on the sides along with the sulphuric acid.

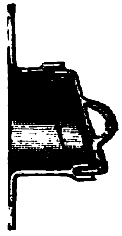
Generally the cylinders of acid-drips are made far too large, so that they show the changes in the process much too slowly. It is therefore preferable in all respects to make the cylinders very small, say holding about 20 cubic centimetres, with a side tube and funnel, into which the fresh drips fall, as shown in fig. 204, whilst the cylinder itself keeps overflowing, and thus its contents are renewed about once in every ten minutes. Special small hydrometers, having only a range of, say, about 20 degrees Twaddell, are made for the purpose of showing the strength of acid in these small drips.

For taking samples of the bottom acid itself a recess is usually made in some part of the chamber by dressing back the lower part of the side. Some, in order to be quite sure, always take the sample out of the chamber itself through a special small man-hole luted with moist clay; in this case there is a slight loss of gas, but no danger of getting stagnant acid. Such a man-hole is shown in fig. 205 in section. The large *man-holes* may be made in exactly the same way; or else their lids may fit into a groove luted with damp clay, as shown in fig. 206. Large chambers are fitted with several acid-drips, man-holes, &c.

For taking the samples themselves a dipper of lead or glass is employed, which is lowered slowly, so as to get all layers of the acid into it. There is often a great difference between the top and bottom acid.

Fig. 205.

Fig. 206.



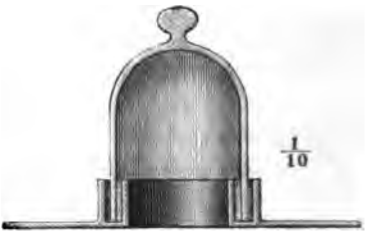
In German works *thermometers* are fixed at regular intervals of 30 to 50 feet in the length of a chamber, whose mercury-vessel is inside, and whose scale is outside the chamber. This means of observing the temperature is undoubtedly infinitely better than the rough one formerly in general use in England, by touching with the hand.

For chambers not exceeding 100 feet in length, one set of drips, thermometers, &c. is generally thought sufficient. For longer chambers this is not the case; at the German works there is generally a special set of these fittings for about every 60 feet length of chamber.

The *pressure* inside the chambers might be indicated by any of the anemometers to be described further on; but usually simpler means are employed, such as ordinary glass pressure-gauges.

Sometimes stoneware plugs are put into holes made in the chamber-sides, in order to indicate the pressure inside the chamber. The tension of the gas is also seen by lifting the lids of the small man-holes (fig. 207), which are always made on the top of the chambers with hydraulic lutes, and which generally consist of glass jars, so as to give light for observation through the side-windows (see p. 510).

Fig. 207.

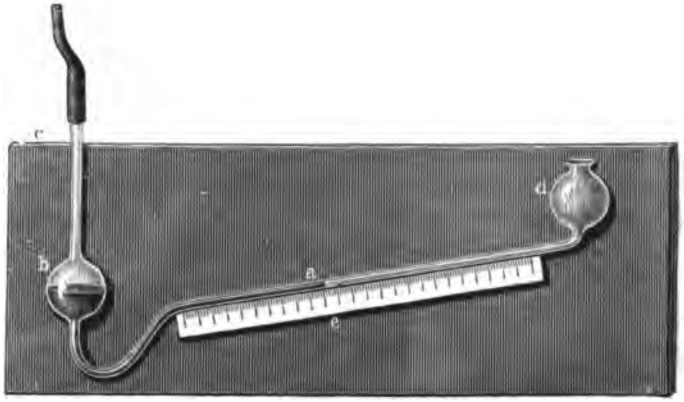


A very sensitive pressure-gauge has been described by Vogt (Journ. f. prakt. Chem. xiv. p. 284). The pressure is observed by the movement of a small air-bubble playing in a horizontal glass tube of 4 or 5 millimetres diameter. The glass tube, besides this bubble, is filled with water or another liquid, and is connected on each side with a bottle tubulated near the bottom. One of these bottles is 15 to 16 centims., the other 6 to 8 centims. wide; the liquid stands at the same level in each.

The pressure within the lead chamber is made to act upon the surface of the liquid in one of the bottles, and its amount measured by the position of the air-bubble. The apparatus is all the more sensitive the greater the difference between the diameter of the tube and that of the bottles. There is a contrivance for admitting a bubble of air previous to using the apparatus, and for again equalizing the levels after use.

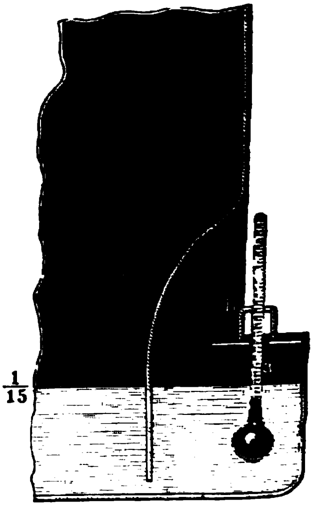
A very simple pressure-gauge, sufficiently sensitive for ordinary purposes, is shown in fig. 208 (from Sorel, 'Industries Chimiques,' p. 142). The tube *a* has an inclination from the level in the proportion of 1 : 10; it is connected with a reservoir *b*, 1½ or 2 inches wide, upon which the pressure is brought to act by the elastic tube *c* (if there is suction, the vessel to be tested must be connected with the bulb *d*). The gauge is filled with a mixture of water and spirit of wine coloured with magenta or otherwise. As the movement of the liquid in the bulb *b* can be neglected, any movement of the liquid in the tube *a*, as measured on the scale *e*, corresponds to one-tenth of its extent in real height. If, for instance, each degree on the scale is $=\frac{1}{10}$ inch, it indicates a real pressure of $\frac{1}{100}$ inch. It is best to cause the liquid to move before each observation, in order to counteract the effect of friction within the tube.

Fig. 208.



For *gauging the height of the acid* there are either stationary lead gauges (which, however, are difficult to read-off exactly), or accurately divided copper rods, which are dipped in every time, but always in the same place, since the chambers are never absolutely level, or glass floats like that shown in fig. 209, the stem, *a*, of which slides in a small lead frame, *b*, whose upper edge serves as an index for reading-off. The float will sink more or less in the acid according to any alterations in its specific gravity. To make this cause of inaccuracy less sensible, the ball of the float is made pretty large. These floats are the most convenient for reading-off.

Fig. 209.



A very great assistance in judging of the chamber-process is afforded by *glass windows* or *sights*, which permit the colour inside the chambers to be seen. Whoever has once got used to these windows will never do without them. They are 8 or 9 inches square, and are placed, at a convenient height for looking through, in those places in the chamber-side which lie in a line with the glass man-hole lids in the chamber-tops; thus they are sufficiently lighted. Where the chambers are roofed in, light must be procured in some other way (for instance, by two opposite windows corresponding with a window in the chamber-shed, &c.). The chamber-glasses are put into small lead rabbets, and luted with white lead and boiled oil. The assertion is occasionally made that the colour of the gaseous mixture, looked at across the width of the chamber, or in the diagonal line from the side to the man-hole lid in the top, is too deep, and that "sights" in the connecting-tubes are preferable; but just the opposite is the case, since the observations are evidently far more accurate, and any alterations of colour much more easily perceived, in the former than in the latter case. Only in the first part is the gaseous mixture, through copious condensation of acid, too opaque for observing its colour; but just there it is quite unnecessary, for only in the back parts of the set is it important to have always an excess of red vapours.

At some works they prefer to the ordinary side-windows, which are rather difficult to keep clean, glass jars, similar to those shown in fig. 207, p. 508, but placed on special short, wide branch-tubes, burnt in the sides of the chambers at convenient places. These jars when dirty can be exchanged in a moment for clean ones, and they are supposed to show all the changes in the chamber-atmosphere quite as well as the glass panes fixed in the lead walls themselves; but my experience is decidedly to the contrary, as sometimes the side jars are quite yellow while the chambers are already pale, and *vice versâ*.

Apparatus for introducing Nitric Acid into the Chambers.

These are divided into two classes. In the first class the nitric acid enters the chambers in a state of *vapour*, mixed with the burner-gas, whose heat evolves it from a mixture of sodium nitrate and sulphuric acid contained in an iron pot. This is styled "potting." In the second class the nitric acid is made in a *liquid* form in special apparatus, and introduced as such into the chambers. Opinions still differ as to which of the two plans is best. The plan of introducing acid in the state of vapour, which is quite general in England but only rarely used on the Continent (in America both processes are found, but the English plan more frequently than the other), has the advantage of greater simplicity and of saving labour and fuel. The advantage sometimes claimed for it, that there is less loss than by making and employing liquid nitric acid, is hardly a real one; for in the first plan some nitric acid is easily condensed during the conveyance of the gas to the chambers, and may corrode brickwork, iron, &c., whilst liquid nitric acid is always introduced exactly in the place where it is needed. It is necessary to employ much more sulphuric acid for the decomposition of the nitrate of soda in "potting" than in the regular manufacture of nitric acid. The presence of nitric acid in the burner-gas will also induce a premature formation of sulphuric acid, especially if it be much cooled; but the Glover tower obviates any inconvenience arising from this. On the other hand, some are afraid that in "potting" the nitre-ovens may get so hot that a portion of the nitric acid will be decomposed down to NO or even to N; but the men generally employ so much sulphuric acid for decomposing the nitre, that this cannot easily happen, nor are NO and N formed so very readily as was formerly supposed (see later on).

The advantages of introducing nitric acid in the ***liquid*** **form** are the following:—avoiding the entrance of false air into the chambers and the escape of burner-gas into the atmosphere, both of which occur in many (not all) systems of employment of gaseous acid; the possibility of employing as much nitric acid and as quickly as desired, whilst in the other case this depends on the heat of the burner-gas, which during a bad process, just when most nitric acid is needed, proves insufficient; lastly, and most of all, the exact regulation possible with liquid nitric acid and its continuous supply, whilst gaseous acid is always given off from the nitre-mixture very unequally. These advantages have induced the great majority of continental manufacturers to adopt liquid nitric acid. Muspratt ('Dictionary of Chemistry,' ii. p. 1029) reports that a continental manufacturer, who previously worked with liquid nitric acid, after having seen the use of solid nitre in England, had saved one third of his nitre by introducing the English plan. This simply proves that that manufacturer had not been very careful before, and is no guide whatever. The opposite experience has been much more frequent. Liquid nitric acid, however, will do harm if the apparatus for introducing it is not constructed in such a way as to completely volatilize it or convert it into gaseous products before it reaches the chamber-bottom, since it will act upon this. Accordingly, sulphur dioxide and aqueous vapour, which decompose the nitric acid, must be brought into as complete contact with it as possible.

It is claimed as an advantage for introducing the nitre by "potting," that the chambers are not exposed to the damage possible with incautious handling of nitric acid, whilst, on the other hand, the irregular evolution of gas from the nitre-mixture is equalized by employing several decomposing apparatus, and charging them in turns, say, once every hour, just after a fresh pyrites-burner has been charged; thus the stronger evolution of nitre-gas runs parallel with that of sulphur dioxide. Some prefer a contrivance for supplying gradually, and not all at once, the sulphuric acid serving for decomposing the nitre. It is contended that the best English works, all of which employ solid nitre, work with as small a consumption of it and as good a yield of vitriol as the best of the continental works employing liquid nitric acid; also on the Continent some manufacturers work quite as well with solid nitre as their neighbours with nitric acid; but it is extremely difficult to check such statements, as few manufacturers divulge their *real* working results to outsiders, and, moreover, very many of them do not even know these results themselves with that degree of accuracy which is required to decide this question.

There is no doubt whatever that the chamber-process can be worked more regularly by the continuous supply of nitric acid in the liquid form (comp. Eschellmann's experiments at Widnes, *infrà*); and the just objection to this, formerly existing, that there was a risk of damaging the first chamber in case of a collapse of the "cascades" (see p. 521) has been entirely removed, in the first place by the almost general plan of introducing the nitric acid into the Glover tower, and in the second instance by spray-producers &c. The labour of making nitric acid in large apparatus and condensing it in receivers is not much greater than that of frequent "potting" on the English plan; the waste of sulphuric acid for decomposing the nitrate of soda is much less in the former than in the latter case, in spite of utilizing the nitre-cake, which pays for the coal consumed in manufacturing nitric acid. The nitric-acid retorts are even sometimes heated by pyrites-burner gases. These reasons explain why the majority of continental manufacturers prefer the employment of liquid nitric acid for the chamber-process, in spite of the somewhat greater "trouble" involved, which, however, is more apparent than real. If all the trouble caused by the English potting-process, in producing a nuisance, running over of the mixture into the kilns, occasional bad decomposition of the nitre, frequent introduction of an excess of air into the chambers, &c., were summed up, it would greatly exceed that involved in making and supplying liquid nitric acid. There remains hardly anything in favour of the English plan except the force of habit and the fear of having some trouble in the transition from one mode of working to another. That the imperfection of the present plan is felt even in England is proved by the various attempts at feeding the chambers with a solution of sodium nitrate, which are irrational in principle and have necessarily failed (see later on).

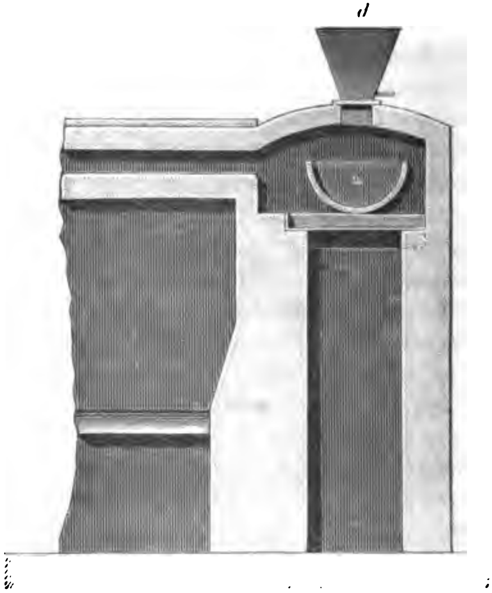
We shall now describe both ways of introducing nitric acid, and begin with the

Introduction of Nitric Acid as Vapour ("Potting").

The apparatus serving for this has been partially described in a former chapter (pp. 270, 279, 311), along with the sulphur- and pyrites-burners. The drawbacks have been pointed out which attend placing the nitre-pots within the burners, or, generally, in such a way that the acid sulphate boiling over can run into the burners. Recently, however, there has always been a special *nitre-oven* constructed by enlarging a suitable place in the gas-flue. It is situated either above or, preferably, just behind the burners, and provided with the necessary working-doors and a cast-iron saucer for collecting what boils over. The nitre-pots themselves have various shapes—for instance, that shown in fig. 210; at *a a* ledges are cast on the bottom, which facilitate pushing the pots backwards and forwards. They hold from 8 to 12 lb. of nitre.

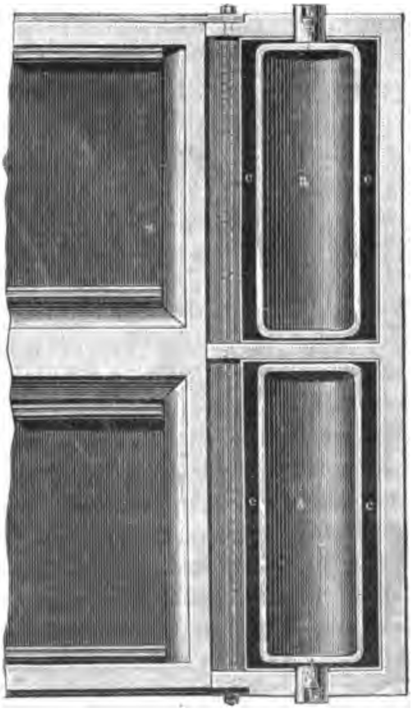
Fig. 210.

Fig. 211.



The "potting" with these pots, which, strange to say, are still (or have been until quite recently) met with in some English works otherwise abreast of the times, is very troublesome and imperfect. During the emptying and refilling of the pots the doors of the nitre-oven are wide open, which does even more harm than in the case of the burners. The heavy pots, along with their melted contents, have to be taken up with long fork-shaped tools and emptied, which requires great strength and skill. The pots, freshly charged with nitre, are placed just within the door of the oven; the necessary acid is poured in from a jug by superficial estimation, and the pot pushed into its place; not till then can the door be closed. If the draught is good, a great deal of air must enter, meeting not even the same resistance as in the burners; if it is not very strong, which will more frequently be the case, so much gas escapes that it can be smelt for some

Fig. 212.



distance. Special dampers would partly obviate this, but are rarely met with. (Such dampers are mentioned in the official Belgian Report of 1855, p. 23.) The pots are quickly worn out, and must be replaced, especially if chamber-acid is employed in them. They last much longer if acid of 140° Tw. is used.

A much more perfect plan is that of decomposing the nitre in a *fixed apparatus*, and running off the acid sulphate (nitre-cake) in a liquid form. This consists of a semicylinder of cast-iron, *a* (figs. 211 & 212), with a cast-on tube *b*, bored somewhat conically. The latter projects out of the nitre-oven, and during the working is closed by a ground-in iron plug with a long handle. Outside there is a cast-iron saucer for holding the nitre-cake, which at once solidifies. The internal saucer, *c*, catches the boilings-over. The nitre is introduced by the hopper, *d*, which is provided with a damper; and after putting in the damper again, it is made gas-tight by filling up with the next charge of nitre. An S-shaped tube (not shown in the diagram) serves for running in the sulphuric acid, for which it is best to provide a small tank with a siphon or stopcock. The acid should be run out of this tank by a pipe with a very fine point into the S-shaped tube, so that the running shall take a long time, and the nitre be only gradually decomposed. Sometimes an iron scraper with a long handle (passing through one of the ends of the oven) serves for stirring up the mixture in the pan. The hole for this must be kept air-tight with clay. An apparatus of the size drawn here holds 56 lb. of nitre, which can be easily decomposed in two hours. In any case there should be two or more of these apparatus, so as to make the current of nitre-gas more regular by charging them in turns.

Even preferable to the arrangement here shown is that of placing the nitre-trough in such a way that the burner-gas can play round the bottom as well. The saucer for the boiling-over stuff, which forms the bottom of the nitre-oven, must then be placed somewhat lower.

At Oker the potting is effected in cast-iron retorts set in the high kilns used there (p. 295); the gas-delivery pipe opens into the gas-flue belonging to the kilns.

Rice (Engl. pat. 16,757, 1892) patents a contrivance which has been in operation in several places for many years past, viz. putting the nitre-oven between the burners and the Glover tower in such a way that, by means of valves, the burner-gas can be made to travel either through the oven or directly into the chambers.

A. P. O'Brien (U.S. P. 694,024) describes a very complicated nitre-oven, the practical results of which are unknown to me.

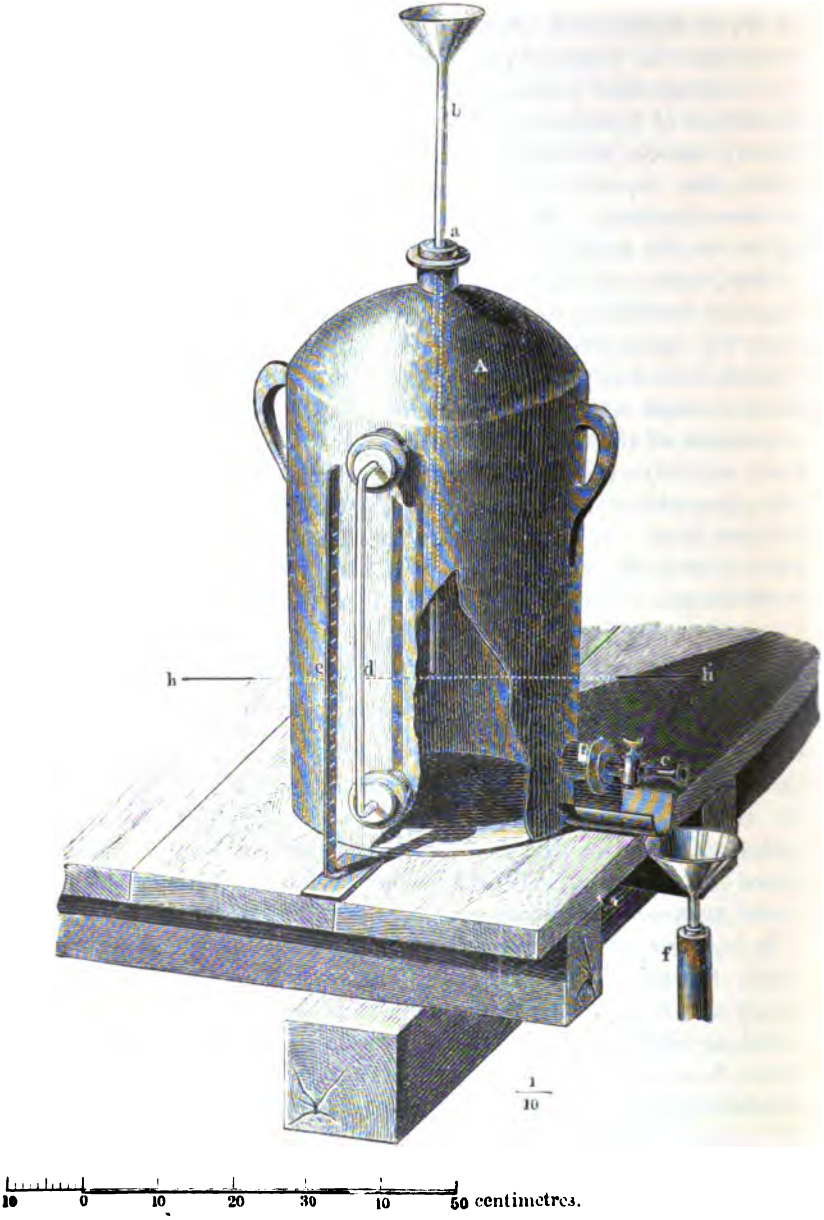
An intermediate process between the "potting" system and the application of liquid nitric acid is the generation of nitric acid in the ordinary retorts, fired with coals (p. 103 *et seq.*), but without condensing the vapours to liquid nitric acid by passing them straight into the chambers. This system, which was followed in several English works about 1880 (Jurisch, 'Schwefelsäurefabrikation,' p. 130), seems to have neither the simplicity and (apparent) cheapness of potting in the nitre-oven, nor the exact regularity of supply by liquid nitric acid. It costs as much coal and very nearly as much labour as the latter; and the passage of the vapours from the nitric-acid retorts to the chambers presents great difficulties on account of the unavoidable comdensation of liquid acid, which is not entirely overcome or rendered harmless by lining the cast-iron pipes with stoneware pipes, with an asphalt or asbestos cement between them. If an acid-maker once emancipates himself (as he ought!) from the old system of "potting," he should proceed to the thorough reform of making and using liquid nitric acid.

Introduction of Liquid Nitric Acid

Any of the apparatus described (p. 103 *et seq.*) may be employed for the manufacture of nitric acid intended for use in vitriol-chambers, but no special precautions are needed for obtaining the acid in a concentrated state or free from lower nitrogen oxides. On the contrary, any low-strength and impure acid obtained in the manufacture of commercial nitric acid may be turned to use in the vitriol-chambers.

It is, however, of the greatest importance for the process to supply the acid in an even, continuous way, and to regulate the supply to a nicety. This can be most simply done by a Mariotte's vessel, as shown in fig. 213 on a scale of $\frac{1}{10}$. The stoneware vessel, A, containing the nitric acid, is closed by a caoutchouc cork, *a*, holding a glass tube, *b*. The latter is the only channel for the air which must take the place of any acid running out through the cock, *c*. As the liquid above the level *h h'*, down to which the tube *b* reaches, is supported by atmospheric pressure, only the

Fig. 213.



height of acid below this can influence the speed of outflow; and this remains constant till the level of the acid has sunk below this point. The glass water-gauge, *d*, and the lead scale, *e*, admit of observing the height of liquid within the vessel. The latter is filled up through the tube *b*, which ends in a funnel at the top. During this either the cork must be raised, or it must be provided with a separate open glass tube which at other times is kept closed. The funnel *f* carries the acid into the glass or stoneware pipes conveying it into the chambers.

At some works there are two tanks which are filled up in turn, one of them every 12 hours, or both every 24 hours. The acid is continually running out of each tank. When one of them is half empty, the other is just full; and thus the variation of pressure is compensated to a certain extent; but this plan cannot at all vie in regularity with a Mariotte's bottle.

The Mariotte bottles sometimes become stopped up by grains of sand &c. getting into the slightly opened stopcock. Bode (Dingl. Journ. vol. 220. p. 538) avoids this by opening the cock full bore, stopping the neck of the bottle tightly by a caoutchouc cork (as shown in fig. 214), through which a tube, *a*, goes down to the desired depth, and is connected by an elastic tube *b* with a metal or glass cock, *c*, of $\frac{1}{8}$ inch bore, which serves for regulating the supply. Further improvements in this apparatus have been made by Liebig (Post's Zeitschr. f. d. chem. Grossgew. 1878, part 2).

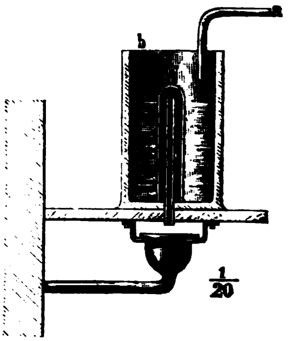
Fig. 214.

Formerly the nitric acid used to be introduced in one or two "tambours" (that is, small lead chambers) about 22 × 10 × 12 feet, or cylinders of 10 to 13 feet diameter and 12 feet height, placed between the burners and the main chamber. The second of these contained the "cascades" or other spreading-apparatus; it stood at a higher level than the first tambour, into which it emptied its acid, and which only served for further exposing it to sulphur dioxide and completely driving off the nitrogen oxides. This first chamber received enough steam to prevent the formation of chamber-crystals, or to decompose them if they arrived in solution from the second chamber; the acid collecting in the first small chamber ran away into the main chamber. The first tambour is unnecessary; with proper regulation the nitric acid can be completely decomposed in the first apparatus by means of SO_2 and steam; but the latter ought to be supplied to such an extent that the sulphuric acid formed contains rather more than four molecules of water to each molecule of acid. At some French works the above-described faulty arrangement of the cascades caused the acid in the second tambour to contain a good deal of nitric acid.

The tambours have been mostly abolished, and the process is carried on in the main chamber; where the nitric acid, as is now usual, is introduced through the Glover tower, the tambours are entirely unnecessary.

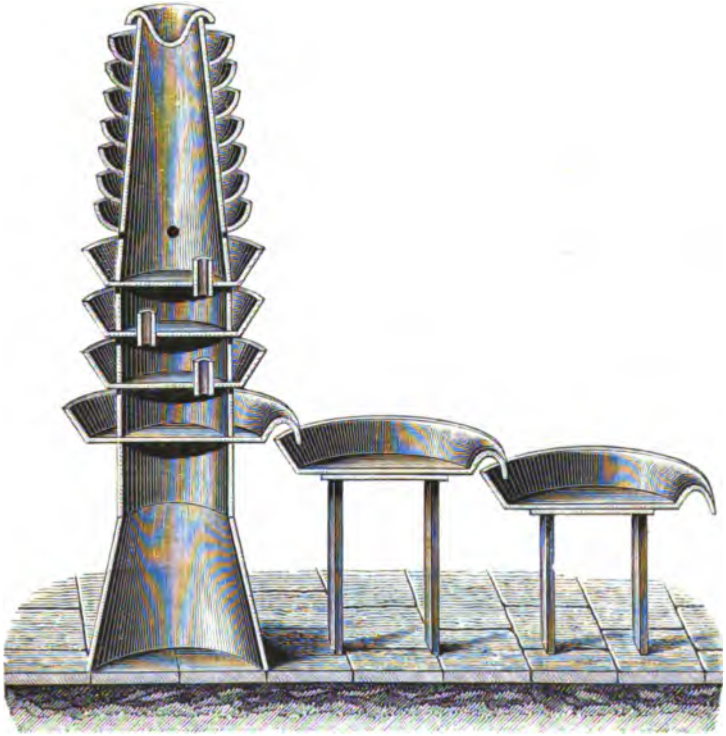
Some manufacturers do not prefer to run the acid continuously in a very small jet, but intermittently in larger quantities. For this a siphon arrangement is mostly employed (fig. 215). *a* conveys nitric acid into the stoneware vessel *b*; through its bottom passes a tube reaching about three-fourths up its height, and open at both ends. This is covered by the wider tube *d*, which is closed at the top and open at the bottom, so that the acid fills up the space between the inner tube and *d*. As soon as it has got to the top of the former, this, along with *d*, forms a siphon which almost directly empties the contents of *d*, whereupon this is slowly filled till the acid has again risen to the top of the inner tube, and so forth.

Fig. 215.



If the nitric acid were simply run into the chambers it would cause very great mischief. It would dissolve in the chamber-acid and quickly destroy the chamber-bottom; moreover, much of it would find its way outside with the chamber-acid without doing its duty within the chambers. It is therefore necessary that no nitric acid should arrive as such at the bottom of the chambers, but that, before reaching there, it should be decomposed into gaseous oxides of nitrogen. This is done by exposing it to the action of sulphur dioxide, that is by the chamber-gases themselves. Before the introduction of the Glover tower, and even long after, no other means were known for this purpose than

Fig. 216.



spreading the nitric acid out over a large surface so that it was thoroughly exposed to the chamber-gases, and nothing could reach the bottom in an undecomposed state. This was done by means of stoneware or glass "cascades," of which there existed many descriptions, which are fully explained and illustrated in the first edition of this work, pp. 308 to 318. Since these cascades have been almost entirely superseded by the Glover towers, we will here show only one of the best descriptions of cascades, that made by Fikentscher, of Zwickau, and shown in fig. 216. The acid run into its top is spread over a large surface before reaching the bottom.

A fault inherent to all such systems is this: that there is no really practical way of knowing whether the nitric acid has been entirely decomposed before the chamber-bottom is reached. The means adopted for this end at some works leave much to be desired.

By far the simplest method of feeding, which dispenses with all cascades, tambours, &c., is that of *running the nitric acid along with the nitrous vitriol through the Glover tower.* Few manufacturers ventured to do this at first, because a loss of nitre was apprehended with this plan; but at most of the best-managed works it has now been done for many years without involving any extra consumption of nitre, and it may be safely asserted that wherever a Glover tower in proper working order exists, no other apparatus is required for feeding the chambers with nitric acid.

This is a principle universally accepted, and borne out not merely by the practice of nearly all sulphuric-acid works where liquid nitric acid is used, and where a Glover tower forms part of the plant, but also by the practice of all the works following the universal English plan of "potting" nitre between the burners and the Glover tower. It is all the stranger that in a modern treatise on the manufacture of sulphuric acid (Jurisch, 'Schwefelsäurefabrikation,' pp. 135 & 153) the old story is repeated of a great loss of nitre in the Glover tower by reduction to N_2O or elementary N, on the strength of some absolutely inconclusive experiments made by Vorster, and refuted 25 years ago by me (comp. Chap. VI.), and of some alleged "experiences" made in the North of France, without any proof by positive data. Wherever figures are given, *e.g.* Hurter's experiments of 1877, Jurisch is compelled to concede that with careful work no more nitre was used after introducing the Glover tower than before.

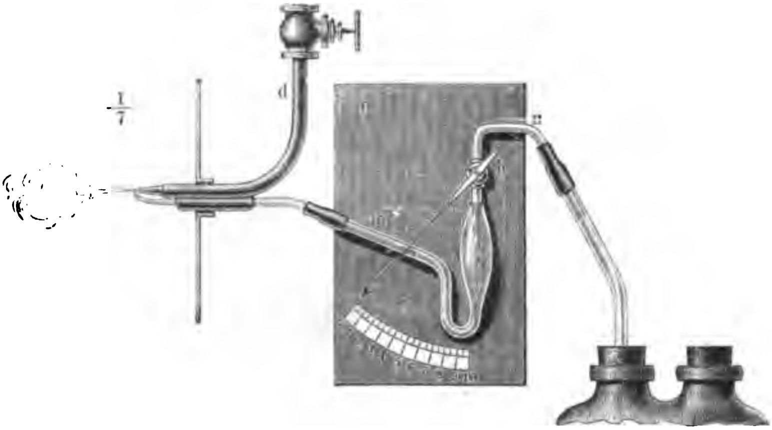
But the *reductio ad absurdum* becomes even more complete by the fact that Jurisch, when speaking of the denitration of nitrous vitriol, states that he decidedly prefers the Glover tower to all other descriptions of apparatus! Seeing that far more nitre passes through the Glover tower in the shape of nitrous vitriol than in that of nitric acid, and that the alleged destructive action of the tower must be precisely the same in both cases, the above is a case of straining at a gnat and swallowing a camel. And this is further illustrated by his remark (p. 156) that the amount of nitre might be to some extent reduced by employing the Glover tower only for treating the chamber-acid and denitrating the Gay-Lussac acid in cascades, ***but that the slight gain in nitre would not pay for the expense of working the cascades*** [which is almost *nil*, so that the "gain in nitre" would amount to the same thing] !

The strangest oversight committed by that obstinate adherence to the exploded idea of the destruction of nitre in the Glover tower is this: wherever the "potting" process is employed, *i. e.* everywhere in England, in the majority of American and in many continental works, the whole of the nitric acid is evolved in the presence of the greatest possible excess of sulphur dioxide and at the highest possible temperature; hence Voster, Hurter, Kuhlmann, Jurisch, and all those who believe in the destructive action of the Glover tower on nitrous vapours, ought to wonder why the greater part of the nitric acid is not reduced to N_2O or N in the ordinary nitre-oven !

Sorel ('Fabrication de l'Acide sulfurique,' 1887, p. 204) states, as the positive result of the experience of the St. Gobain works, that there is *no* destruction of nitric acid in the Glover tower.

Since in exceptional cases a Glover tower is not available for

Fig. 217.



the introduction of nitric acid, we shall describe a very efficient spray-apparatus, constructed for this purpose by M. Liebig

(Zeitsch. des Vereins deutscher Ingenieure, 1879, p. 111). It consists of a lead steam-pipe *d* (fig. 217) with a platinum nozzle,

Fig. 218

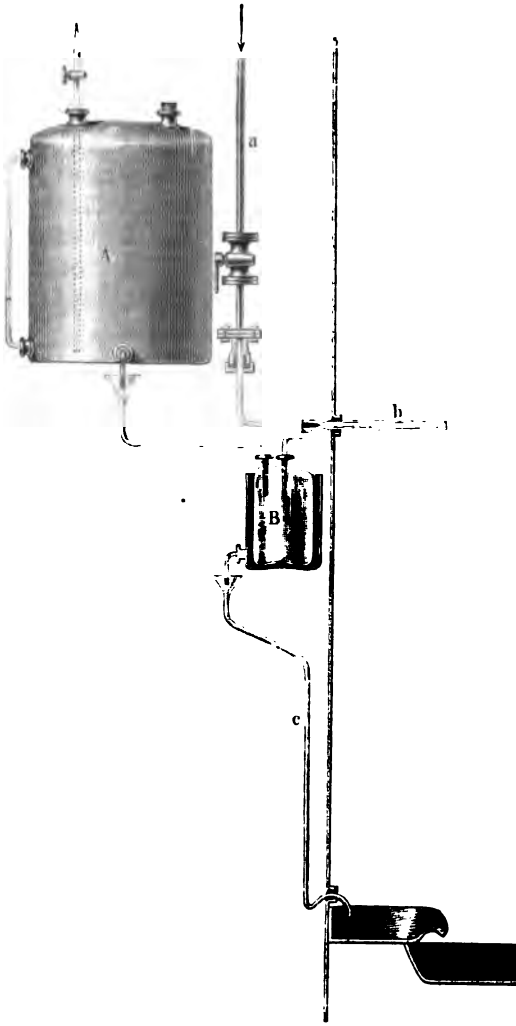
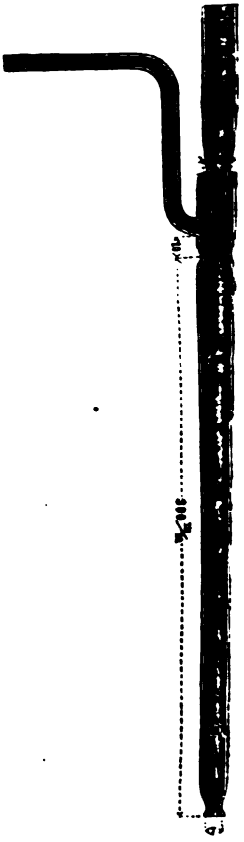


Fig. 219.



parallel to which runs a glass pipe *m*, for conveying the nitric acid, bent up in front and drawn out into a fine point. The steam rushing past this causes a vacuum in the glass tube, and sucks acid through the latter from a stock-bottle, a glass cock *h* regulating the supply. The acid is divided into a fine mist, and none of it arrives at the bottom undecomposed.

An apparatus for the same purpose, constructed by Mr. Stroof, of the Griesheim works, has been made known to me by that gentleman, and is illustrated by figs. 218 & 219.

Fig. 218 shows the general disposition, fig. 219 the details of the injector *b*. The nitric acid runs from a Mariotte's bottle A into a Woulfe's bottle B, standing in a glass dish, provided with an overflow-pipe *c*, which conveys the acid, in case of the injector breaking down, on to the cascade C. From the bottle B the acid is sucked away by the glass injector *b*, whose steam-jet is connected with the steam-pipe *a* by a stuffing-box. Such injectors are best made of well-annealed water-gauge pipes, drawn out to a point. The point projects but loosely into the suction-pipe, so that a little air is sucked in as well, and no breakage can take place by expansion. At a pressure of 1½ atm. the injector can carry away 16 cwt. of nitric acid in 24 hours in the form of spray, along with a little air. The mouth-piece of the injector must be contracted and widened out again, like that of a fire-engine, to prevent any larger drops forming at that place. The acid is thus completely converted into a mist, and a sensible saving effected in comparison with cascades.

Another glass injector for nitric acid has been described by Burgemeister (Fischer's Jahresb. 1880, p. 228). He employs a platinum nozzle (*not* soldered with gold!) and a steam-jet placed just below, the latter consisting of a platinum nozzle, about ⅛ inch wide, inside the chamber, continued outside into a copper tube. Both tubes pass through a lead pipe burnt into the chamber-side, and are fastened in this with glycerine-lead cement.

At the Freiberg works, where, in consequence of the complete cooling of the roasting-gases, they do not employ a Glover tower, formerly the nitric acid was introduced by cascades. These have been replaced by glass injectors, constructed by Wolf, as shown in fig. 220 & 221. A glass tube, a^1, 28 mm. wide, is sealed to a narrower central tube, a^2, at the place *a*. At *b* there are three glass knobs for steadying the inner tube a^2, and at *c* four small glass knobs for steadying the platinum capillary *d*. Tube a^1 is provided with a funnel *e* for running in the nitric acid. The tube *d*, made of platinum-iridium, is connected with a steam-pipe and is held in the centre of pipe a^2 by an india-rubber cork *f* and the knobs *c*, *c*. The outlet of a^1 is 6 or 7 mm. wide. The nitric acid flows through *e* into the annular space between a^1 and a^2 and is sprayed into the chamber by the steam issuing through the platinum capillary. The whole is inserted into the chamber-side by means of an india-rubber joint at *g*, so that it is easily taken out and cleaned.

Fig. 220.

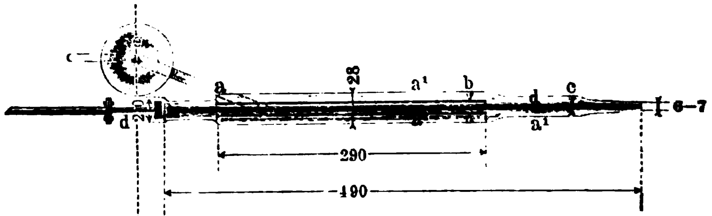
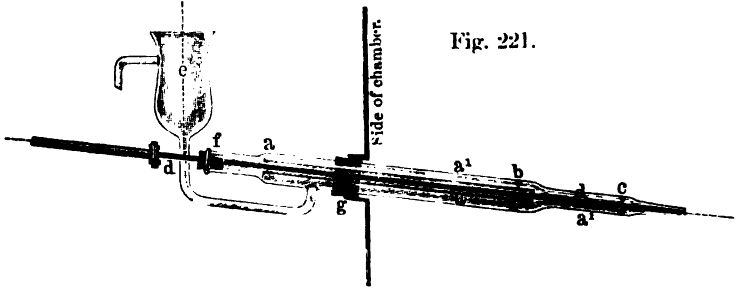


Fig. 221.



Potut (G. P. 122,920) introduces the nitric acid (or nitrate of soda solution, comp. later on) by a steam injector into the pipe leading from the Glover tower to the first chamber, with the ridiculous assertion that thus two-thirds of the nitre are saved in comparison with running the nitric acid down the Glover tower or straight into the first chamber.

Other manufacturers inject nitric acid into the last chamber (comp. next Chapter).

The simplest way of introducing the nitric acid through the Glover tower is to run a suitable quantity of it into the nitrous-vitriol tank at the bottom of the tower, and pump up the mixture in the usual manner. It is sometimes preferred to carry the nitric acid to the top of the chambers or the tower, and so run it into one of the lutes of the tower as required.

The storing of nitric acid on the top of the chambers or of the Glover tower is generally effected in large stoneware receivers, or else in a number of smaller stoneware jars or ordinary glass carboys, all of which are connected by glass siphons, so that the running off by means of a tap-siphon need take place only from the last vessel of the set (fig. 222). Vessels proof against nitric acid may also be composed of single pieces of stone joined together by a cement made of finely-ground asbestos and a dilute solution of silicate of soda, kneaded into a putty and preferably mixed with ground sulphate of baryta.

Fig. 222.

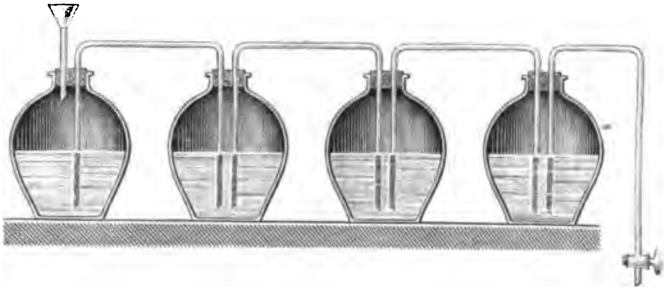
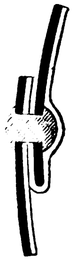


Fig. 223.



E. Pohl (G. P. 30,188) employs iron vessels lined inside with asbestos cloth soaked in paraffin. The riveting of the iron shell is effected in the manner shown in fig. 223, so that the acid nowhere comes into contact with the iron.

Introducing Nitre as an Aqueous Solution of Nitrate of Soda.

There is yet a third way of introducing the nitre. Many years ago several works ran their nitre as a *solution in water* into the chambers. This has long since been discontinued, both because sodium sulphate gets into the acid, which is not allowable for many purposes, and because the lead always wears away very quickly at the point where the solution enters. The same method was patented by Burnard (14th Aug., 1875). The solution of nitre was to be injected into the chamber in a thin jet, or, better still, at once mixed with sulphuric acid by means of a steam-jet, exactly similar to Sprengel's water-spray (*vide infrà*). The chief object sought to be attained in this process was an imaginary saving of nitric acid, which in the decomposition of nitre by the burner-gas was supposed to be reduced to N_2O and N. It has been shown on p. 522, and will again be referred to in Chapter VI., that no sensible decomposition of this kind takes place at all; and any advantage accruing therefrom would be far more than counterbalanced by the difficulty of keeping the nitre solution long enough in suspension to completely decompose it and to prevent liquid nitric acid from getting at the chamber-bottom. The process also takes so much steam that the acid in the first chamber gets too weak. This is certainly contradicted by the patentees (Chem. News, xxxvii. p. 203); but no independent favourable testimony has yet been published, and a saving of nitre appears out of the question. It would, however, seem feasible to run a solution of nitre through the Glover tower along with chamber-acid and nitrous vitriol, so that the nitre would be decomposed in the tower itself, sodium sulphate and nitrous vapours being formed. Of course this plan, as well as that mentioned before, is restricted to the case of all the sulphuric acid being intended for decomposing salt, or for the manufacture of superphosphates, &c.

The last-mentioned plan is undoubtedly the simplest imaginable for introducing the nitre, uniting the advantages of both solid nitre and nitric acid—easy regulation, introduction of any quantity at a time, dispensing with all apparatus for introducing the nitre or manufacturing nitric acid, saving of labour and coals (in the case of nitric acid), avoiding the handling of nitric-acid carboys or of fluxed nitre-cake, the latter being an article difficult to utilize to any extent. Unfortunately these advantages are counterbalanced by a drawback, which has induced most manufacturers who have tried this process to give it up: it is found that sodium sulphate crystallizes in the towers, tanks, and connecting-pipes and causes obstructions. It would be necessary to have two Glover towers for each set, and to run the nitre solution down only one of these, whose acid would not be used for the Gay-Lussac tower, but for the salt-cake pans or for superphosphate only. This would be very inconvenient, and for smaller works not at all feasible.

Blinkhorn (E. P. 1084, 1878) runs a solution of sodium nitrate, of spec. grav. 1·35, in a regular jet upon sulphuric acid contained in a pot heated by the burner-gas, and draws off the solution of sodium sulphate from time to time. This will hardly decompose all the nitrate!

Potut (B. P. 7710, 1900) injects a solution of sodium nitrate between the Glover tower and the first chamber (comp. p. 526).

Feeding the Chambers with Nitrous Gases obtained as By-products.

Several proposals partly carried out in practice have had no lasting success. Thus, for instance, the attempt has been made in France to obtain *oxalic acid* as a by-product in evolving the nitre gas by heating molasses with nitric acid and conducting the vapours into the chambers. The yield of oxalic acid, however, was not large enough to compete with its manufacture from sawdust by fusing caustic potash. Not more successful was a proposal of Laing and Cossins, to heat sodium nitrate with arsenious acid or chromium oxide, in order to obtain arseniates or chromates along with nitrous acid for the chamber-process (Wagner's Jahresb. 1862, p. 207). It is also quite feasible to convey any nitrous gas generated in making arsenic, antimonic, phthalic acid, &c. by means of nitric acid, which formerly used to be lost, into the lead chambers; but this process, which (like all similar ones) can hardly be so conducted as to give a sufficiently *regular* supply of nitre to the chambers, is no longer called for, since the respective works now regularly regenerate nearly the whole of the nitric acid by mere contact of the vapours with an excess of air and water in "plate-towers" or similar apparatus (comp. p. 125 *et seq.*).

An ingenious process, invented by Dunlop, was for many years carried out at St. Rollox, but it has not been used at the new works at Hebburn belonging to the same firm. A mixture of common salt, nitrate of soda, and sulphuric acid is heated in large iron cylinders; the principal reaction setting in is as follows:—

$$3SO_4H_2 + 2NaNO_3 + 4NaCl = 3Na_2SO_4 + N_2O_3 + 4Cl + 3H_2O;$$

but the further deoxidation of nitric acid will only be prevented by keeping within certain limits of temperature. Thus there remains a soluble residue of sodium sulphate, whilst chlorine and nitrous acid are given off in a gaseous state. The two gases are separated by passing them through a series of leaden Woulfe's bottles filled with sulphuric acid of 1·75 spec. grav., which retains the nitre-gas, being converted into "nitrous vitriol" and used as such (*vide infrà*); the chlorine passes through without absorption and is utilized for bleaching-powder. The advantage of this process is, that chlorine is obtained direct from salt without making any hydrochloric acid and without wasting manganese. The drawbacks are:—that the nitre-gas has to be evolved again from the nitrous vitriol, which at that time could only be done by diluting with hot water, necessitating a reconcentration of the vitriol; that there is a danger of losing nitrogen compounds; and that the apparatus is very complicated. This process consequently did not obtain permanent success.

At the Uetikon works, near Zurich, nearly all the nitre required for the chambers is obtained in the manufacture of *iron mordant* for dyeing purposes. This is made by treating ferrous sulphate with nitric acid, and thus oxidizing the ferrous to ferric sulphate. The nitric acid is thereby reduced mostly to lower oxides of nitrogen; these gases are conveyed into the vitriol-chambers, and there do exactly the same duty as if the nitric acid had been directly supplied to the chambers. Recently the manufacture of *cupric sulphate* from metallic copper, sulphuric and nitric acid has been introduced at the same works, equally carrying all the nitrous vapours into the vitriol-chambers.

Supply of Water as Steam or Spray.

The water required to produce H_2SO_4 and to dilute this to the point required for the practical working of the chambers must be presented to the gases in as fine a state of division as possible. This was formerly in all cases and is still generally effected by injecting into the chamber a certain quantity of *steam,* which rushes forward and on its way is condensed to a mist of very fine particles of liquid water. At many works, however, water is now injected in the shape of a mechanically produced spray.

The Steam

is always generated in an ordinary steam-boiler, since boilers placed above the sulphur-burners have been given up everywhere. The boilers are constructed in the usual manner, but are mostly made for low pressure, rarely working above two atmospheres, more frequently only at one or one and a half atmosphere; in the south of France they work at three or three and a half atmospheres. A high pressure has no object so long as the liquid is spread over the whole chamber-space; for even low-pressure steam fulfils this requirement and sufficiently assists the draught. Low-pressure steam is more easily kept at a uniform tension than high-pressure: without this no regulation of the supply of steam to the chambers by the attendant is of any avail. High-pressure steam certainly condenses less readily than low-pressure steam; but this is a doubtful advantage, so long as the steam possesses enough "carrying-power" to convey the minute globules of water right to the other end of the chamber. Experience has shown that this is the case even with low-pressure steam; at most English works they employ only a single jet at one end of each chamber, and consider this quite sufficient to supply the whole chamber with moisture, but I do not like this practice (see p. 534).

Of course low-pressure steam may be obtained from a boiler working at high pressure by means of a reducing-valve. Thus at the Oker works the steam-pressure in the boilers is 3 to 3·5 atmospheres, and is reduced to 1 to 1·5 atmosphere for feeding the chambers. At small works the same boiler may be utilized for supplying the chambers and for driving the machinery of stone-breakers, air-pumps, and so forth.

It is also almost a matter of course that the chambers may be fed with the exhaust-steam of engines, if these are worked in such a way as to leave some pressure in the exhaust. The utilization of the waste steam of the Gay-Lussac air-pump for this purpose had been practised by myself for many years, as described in the first edition of this work (1879), vol. i. pp. 393 & 565. A proposal not essentially differing from this was patented much later by Sprengel (No. 10,798, 1886).

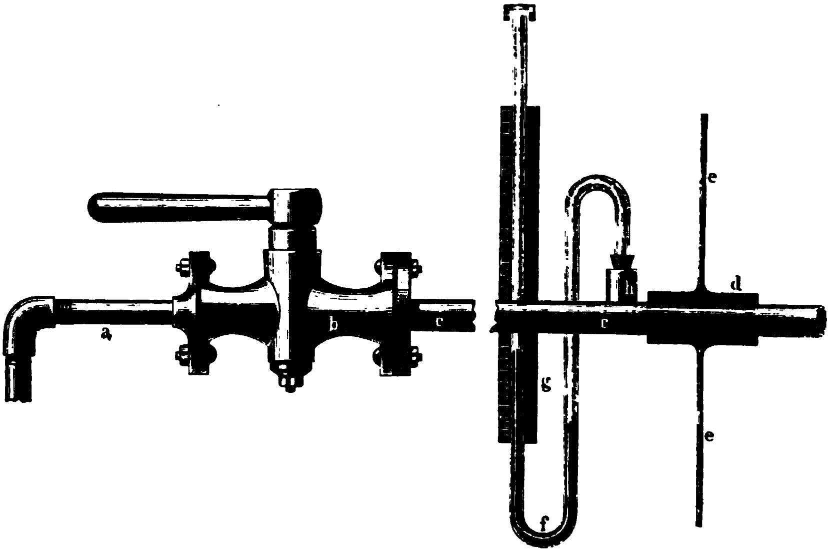
At some large works, in order to control the uniform tension of the steam, so important for the regularity of the chamber process, *registering steam-gauges* are employed, which show the tension during the whole day on a sheet of paper wrapped round a drum making one revolution in twenty-four hours. Such a gauge, made by Schaeffer and Budenberg, of Magdeburg, is described in 'Dingler's Journal,' ccxxvii. p. 519.

The *conveyance of the steam* to the chambers usually takes place in cast-iron pipes, with one or more branches for each chamber. The main-pipes in any case, and, if possible, also the branch-pipes, considering their great length, should be surrounded by bad conductors of heat to restrict radiation as much as possible, and avoid a considerable loss by condensation of water.

The pipes must always be laid with a slight fall towards the boiler, so that the condensed water may run back. Where, from local circumstances, this cannot be done, automatic apparatus for removing the water should be fixed at the lowest points.

Of course the size of the main-pipes must correspond to the number and size of the chambers. When more than one steam-boiler is required, they are placed together and their main-pipes connected so as to equalize the pressure. The *branches* for each chamber need not be above 1 inch wide, even for large chambers (up to 70,000 cubic feet) supplied by one jet. They are made of wrought-iron tubes, *a* (fig. 224), sometimes of copper, up to a short distance from the chamber, where they end in a cock or valve, *b*, to which a lead pipe, *c*, equal in width to *a*, is attached and projects into the chamber itself. It is not, however, burnt to the chamber-side, *e*; but a short wider tube, *d*, is burnt to this, and *c* is loosely put into it, the joint being made tight with tar, cement, &c. Sometimes in lieu of this an india-rubber cork is employed, but this does not last long. In the latter case, if the outlet is stopped up by lead sulphate, the pipe *c* can easily be drawn out and cleaned and no platinum nozzles are required (as had been proposed by Scheurer-Kestner).

Fig. 224.



The same figure shows another commendable contrivance, viz. a simple mercurial *pressure-gauge*, consisting of a bent glass tube, *f*, with a scale, *g*, connected by means of a caoutchouc bung with a branch, *h*, of the lead pipe *c*. Thus the pressure *behind* the regulating-cock can be observed at any time; and the chamber-manager has thus a means of very accurately regulating the supply of steam. Any water condensed in the gauge can be easily allowed for.

A good *steam-cock* is preferable to a wheel-valve, because the wheel does not show how far the valve is opened, whilst the handle of the cock can be fitted with a graduated arc so that its position can be fixed with precision.

Automatic steam-regulators, if reliable, save a great deal of trouble, but do not dispense with constant supervision on the part of the attendant, as they are somewhat liable to get out of order.

In England the usual way is, or formerly was, this: to employ only one jet of steam for each chamber, mostly beside, above, below, or even within the pipe conveying the gas from the burners, the Glover tower, or the preceding chamber. Some introduce the steam quite near the top, others in the centre of the chamber-end. A single steam-jet suffices, if the length of the chamber does not exceed about 130 feet; in longer chambers it would not carry right through.

It is maintained by English practical men that a single steam-jet from a 1-inch pipe is quite sufficient for feeding chambers up to 130 feet length, and also that the distribution of moisture through the chambers is thus properly effected. By arranging a single steam-jet, the cost of cocks, branches, &c. is saved, and the regulation of the supply of steam is much simpler and easier than if, for instance, four cocks were to be opened a quarter as much as the cock of a single jet. It is also true that in this way the front part of each chamber, which makes most acid and evidently requires the greatest supply of moisture, actually receives it; but this does not hold good of the first chamber, which obtains a considerable portion of its steam from the Glover tower, so that a steam-jet placed in the just described way is certainly not in the right position. The steam-jet should enter the chamber near the top, or at least in the upper part of the side. Experience has shown that it is not advisable to send the steam into the lower portion of the chamber.

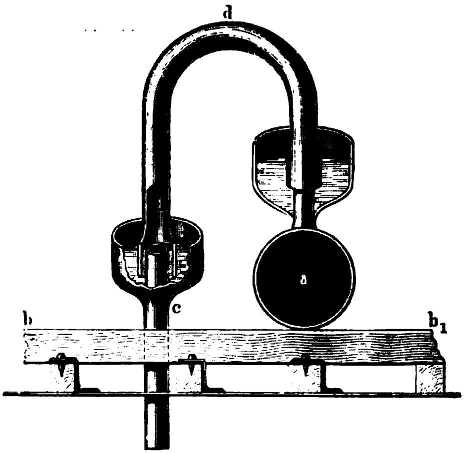
Most experienced managers, however, now agree that the single steam-jet for each chamber is a faulty appliance. The chamber should not be left to haphazard supply of its different parts with the necessary amount of moisture, but each part should receive just what it needs.

On the Continent, indeed, most manufacturers have always preferred employing a number of steam-jets for each chamber, so as to make themselves independent of any casualties in the proper distribution of steam by a single jet. These branch jets are introduced at right angles to the direction of the gaseous current either in the long chamber-sides, not far from the top, or, which is most usual, through the roof of the chamber, so that the single jets can be regulated by a man walking over the top. Thus, for instance, at the Oker works there is a steam-pipe extending above the chambers, from which, at intervals of 17 feet, branches of ⅜-inch bore enter the latter; from these the steam issues, by several small openings immediately below the top, in several directions (Bräuning, Preuss. Zeitsch. 1877, p. 137). A similar arrangement exists at Aussig and elsewhere. In all these cases each branch-cock must be regulated separately.

Where a Glover tower is in use, the first steam-jet should not be in front of the first or "leading" chamber, as this part receives enough steam from the Glover tower; the first steam-jet should be 20 or 30 feet, or even farther, from the front side.

An apparatus by which steam can be introduced at many places and yet regulated at a single point has been described by Scheurer-Kestner (Wurtz, Dict. de Chimie, iii. p. 149); it is shown in fig. 225: *a* is the copper main-pipe running in the centre of the chamber-top, and held fast by the joist b b_1, as well as the branches *c*. The latter are arranged alternately on the left and right hand at distances of 16½ feet; they are made of lead, pass through the chamber-top, and are burnt into it. The arm *d*, covered with straw rope, serves for making the communication between *a* and *c*. Both pipes have hydraulic lutes, so that only a very low pressure can be employed. The main-pipe, *a*, is provided with a cock, and the supply of steam regulated by this. The steam, entering the pipe at the front end of the chamber, will principally escape through the first branches, where it is most needed, because in the beginning a large quantity of unchanged sulphur dioxide is present. The pipe *a* has sufficient fall for emptying the condensed water. (This arrangement seems to offer no advantage over simple branches on a main-pipe, and has the great drawback that only a very low pressure can be employed, as the water is easily thrown out of the hydraulic joints *a* and *c*. Moreover, it disregards the necessity of supplying the various parts of the chamber with different amounts of steam.)

Fig. 225.



Perfectly absurd is the arrangement given in every edition of Payen's 'Précis,' even up to the last one (1877), and copied from it into many other treatises. Here the steam-jets are shown partly in the chamber-bottom, coming through the chamber-acid. No practical man can imagine that this plan, if it has been actually carried out anywhere, has not been discontinued at the first opportunity; for the shaking by the steam must gradually cause a leakage at the joint, which cannot be got at, owing to the chamber-floor, nor can it be repaired till the chamber has been entirely emptied.

The total quantity of steam required for a set of chambers, which should be known approximately in order to fix upon the boiler-space and the size of the main-pipes, of course depends, first, upon the quantity of sulphur to be burnt, secondly upon the existence of a Glover tower, and thirdly upon the strength to which the acid is brought in the chambers. A general rule, therefore, cannot be laid down. The two latter conditions are partly reciprocal; the stronger the acid is made in the chambers, the less water is evaporated in the Glover tower, and *vice versâ*. If we assume, adopting a proportion very usual in England, that all the chamber-acid is brought up to 124° Tw., and that it is concentrated in the Glover tower up to 148° Tw., the amount of steam required will be as follows:—

Each pound of sulphur burnt requires,

1st, for forming $\frac{98}{32}$ SO_4H_2, $\frac{18}{32}$ water ...... $=0{\cdot}5625$ lb.

2nd, for diluting it down to 124° Tw. ($=70$ per cent. SO_4H_2), $\frac{30 \times 98}{70 \times 32}$ ...... $=1{\cdot}3125$ „

$1{\cdot}8750$ „

Of this nothing is lost with the escaping gas, as this passes in the Gay-Lussac tower through strong vitriol; on the contrary, the Glover tower saves the steam corresponding to a concentration from

124° ($=70$ per cent.) to 148° Tw. ($=80$ per cent.), viz. $\frac{10 \times 98}{70 \times 32}$ .... $=0{\cdot}4375$ lb.

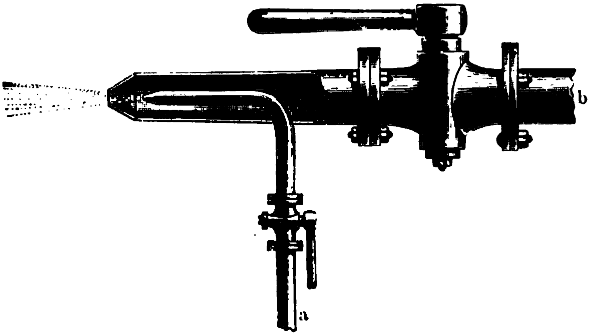
Leaving.............. $1{\cdot}4375$ lb.

which must be supplied to the chambers. To this must be added a certain quantity for water condensing in the steam-pipes; but this cannot be estimated generally, since here everything depends upon the length of the pipes, their thickness, surroundings, &c. On the Continent the chamber-acid is kept more dilute and correspondingly more steam is used. It is safe to say that the steam to be generated in the boiler, without a Glover tower, amounts to about 2½ times—with it, to about twice the weight of sulphur burnt.

Employment of Water in the form of Spray.

Instead of feeding the chambers with steam, Sprengel (patent of October 1st, 1873) proposed liquid water in the form of a fine spray. His reasons are these:—that the steam increases the volume of the gases by its heat, and consequently more chamber-space and nitre are required, which can be avoided by introducing the water in a liquid form, sufficiently divided; and that the cost of evaporation can be saved in this way. The water is made into a spray by the employment of steam, a steam-jet of 30 lb. tension escaping through a platinum nozzle in the centre of a water-jet, as shown in fig. 226 (where *a* is the steam-pipe, *b* the water-pipe); 20 lb. of steam is sufficient for converting 80 lb. of water into a mist. Such jets are arranged in the chamber-sides, at distances of 40 feet apart, and supplied with water from a tank fixed at some height above. Sprengel assumed that two-thirds of the coal can be saved in this way, instancing the works at Barking Creek, where at the same time a saving of 6½ per cent. pyrites and of 14¾ per cent. nitre is said to have been effected. At those works there was no Gay-Lussac or Glover tower. In the case of factories working with a Glover tower, Sprengel estimated the saving in coal at a third less (Chem. News, xxxii. p. 150). Of course the water- and steam-cocks must be exactly regulated, and the two nozzles must have a particular shape, so that only a fine mist and no larger drops shall be formed, which would at once fall to the bottom and only dilute the chamber-acid.

Fig. 226.



A different way of producing a spray or mist of water instead of a steam-jet for feeding vitriol-chambers is employed at the Griesheim works, and has thence been introduced with great success into several other factories. The spray is here not produced by the injection of steam, but by allowing the water, at a pressure of two atmospheres, to issue from a small platinum jet against a small platinum disc. Two rows of such water-jets are introduced through tubes in the chamber-top, each tube about 20 feet away from the other. Thus the whole chamber is uniformly filled with a fine mist, which, together with the steam coming from the Glover tower, supplies all the water required for the chamber-process. The water must be carefully filtered, as otherwise the jets would soon be stopped up; but this trouble is far more than compensated by the considerable saving in fuel caused by doing away with the chamber boilers. The fear formerly entertained, that the introduction of the moisture in the shape of liquid water would reduce the temperature of the chambers below that most favourable for the acid-making process, is entirely groundless. At Griesheim it was noticed that the temperature of the gases, arriving from the Glover tower sometimes at only 35° C., quickly rose within the chambers to 50° C. Similar observations have been frequently made, most extensively by Lunge and Naef (comp. Chap. VII.). This is explained by the fact that the evolution of heat, consequent upon the chemical reactions going on within the chamber, is far more important than the heat brought in by the steam, and that, in fact, the local cooling produced by the water being supplied in the liquid form is actually beneficial in most cases.

It might be objected to the introduction of the water in the shape of a spray, that steam is preferable on account of being only gradually condensed in its onward course within the chamber, and that the moisture would thus be more uniformly distributed through the chamber. But this objection is not at all valid, and would not be so even if no sulphuric acid were present in the chamber. Calculation shows that the gas introduced for each kilogram of sulphur, whose volume at 50° C. and 760 millim. pressure amounts to 8345 litres, can contain only 0·6868 kilogram of aqueous vapour, whilst the total amount of water is nearly four times as much, and three-fourths of the steam entering into the chamber must therefore be at once condensed into water. This calculation, given in our 1st edition, pp. 348 & 349, is not repeated here, since it does not take into account the fact that the tension of aqueous vapour within the chamber is very much reduced by the presence of sulphuric acid, and it is hence useless for our purpose. Hurter (J. Soc. Chem. Ind. 1882, p. 51) somewhat more correctly applies to our case Regnault's table for the tension of aqueous vapour in sulphuric acid of various strengths, and he there gives a diagram which allows of finding this tension for any intermediate concentration of acid. But this is incorrect for the principal working part of the vitriol-chamber; for Regnault's determinations only go as far as 35° C., that is much below the ordinary chamber-temperature, and it is not admissible to calculate tensions at 60°, 80°, or even higher temperatures by simply applying Regnault's table or Hurter's diagram to them. This gap has been filled by a set of elaborate observations made by Sorel, and first rendered accessible to the public by me (Zeitsch. f. angew. Ch. 1889, p. 272). Sorel's table extends to acids from 44 to 82 per cent. H_2SO_4, and to temperatures from 10° to 95°. We have given it in the third Chapter, p. 196, where the specific gravities corresponding to the acid percentages have been added for the reader's convenience. At the close of this Chapter we shall give a table for reducing volumes of gases to the conditions of the vitriol-chamber atmosphere, which equally takes into account the aqueous-vapour tensions of sulphuric acids of various strengths.

The importance of this table will be indicated at present by only one example. In a special instance the temperature close to the chamber-side was 80°; the acid running down the side stood at 114° Tw.$=$66 per cent. H_2SO_4, and the aqueous-vapour tension at this place was, therefore, $=$39 millim. Only 6 centim. (say 2½ inches) within the chamber the temperature was already 95°; but at this temperature an acid, whose aqueous-vapour tension is$=$39 millim., must have a strength of 128½° Tw.$=$72·33 per cent. H_2SO_4, and this was found to be really the case. We shall see the importance of this in Chapter VII.

Looking at the great reduction of the tension of aqueous vapour by the presence of sulphuric acid, we must conclude that the steam introduced into the chamber must be condensed almost immediately into a liquid mist, and this must reduce the alleged superiority of steam in "carrying power" to a properly comminuted spray of water, introduced at high pressure, to almost *nil.*

Of course the water *must* be properly comminuted; otherwise, that is when it drops from the jets in the shape of rain, it dilutes the chamber-acid to an intolerable degree, and this is all the more injurious as this dilute acid floats on the top of the stronger chamber-acid, and is not noticed for a long time at the places where the acid is drawn off, till it becomes too late to meet the evil at once. This accident will happen whenever the jets are out

Fig. 227.

Fig. 228.

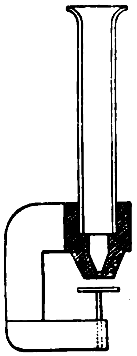


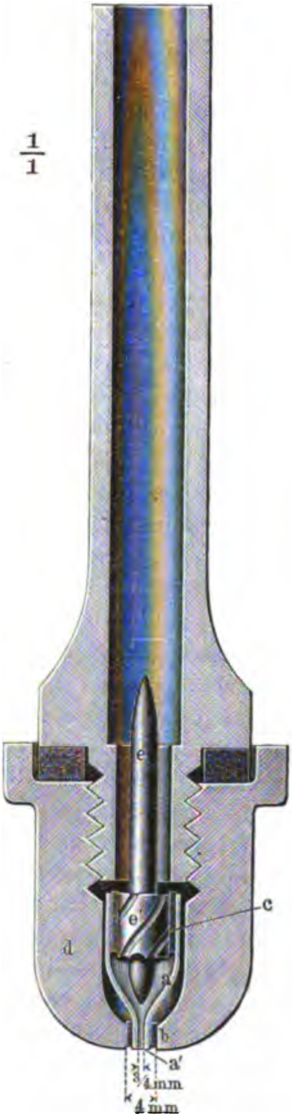
Fig. 229.

of order, and this has, very unnecessarily, caused several works to abandon the plan of introducing the water in the shape of a liquid spray.

A special platinum jet for converting water or acid liquids into a thin spray has been constructed by F. Benker, of Paris, and is shown in fig. 227. In this jet the distance between the nozzle *a* and the disc *b* is adjustable, the disc being moved backwards or forwards by means of a rod, at the end of which is cut a fine thread, which works in a similar nut *c*, placed on the top of the cylinder. The screw and nut are made of an alloy of platinum and iridium, so that there is no fear of their wearing out. In this manner the best distance between *a* and *b* can be easily attained, and by removing *b* altogether the nozzle *a* is easily cleaned. More recently Benker has employed spray-producers of the shape shown in fig. 228, with the platinum-iridium jet cased in antimony-lead, and without an adjusting-screw.

Körting Brothers' spray-producer (fig. 229) (Zeitsch. f. angw. Chem. 1888, p. 404) contains within the contracted part a metal spiral, which by the pressure of the liquid is kept tightly in its place, whilst the liquid on passing through the helicoidal channel takes a rotating movement, so that, on issuing, it is projected equally on all sides as a conical spray. The nozzle and spiral spring can be arranged for spray of any degree of fineness. This apparatus was originally intended for damping the air in cotton-mills &c. for precipitating dust, for absorbing acid vapours, and so forth. It has also been made of platinum, and is in several places used for producing a fine spray of water in vitriol-chambers.

Fig. 230.



These Körting's spray-producers ("Streudüsen") were also made of antimony-lead with a platinum lining, but this did not stand the corrosion in acid-chambers, and had to be replaced by solid platinum nozzles. Even these do not last so long as nozzles made of glass, as shown in fig. 230. The glass tube *a* is drawn out to a capillary point at *a'*, where it is cut off quite straight so that the jet of water comes out centrally, not sideways; in 24 hours 900 or 1000 litres of water should be delivered from this. This glass nozzle is fixed in the antimony-lead part *d* by means of a thin india-rubber washer *b*, the joint being made tight by the water pressure, and both orifices being at the same level. Within *a* the Körting spiral *e*, made of gun-metal (this metal can be employed, as no acid penetrates here), is fixed by the thick india-rubber tube *c*. This apparatus is set in the chamber-top in such a way that the jet comes out horizontally, and that the whole can be removed at will for the purpose of cleaning or inserting a new glass nozzle.

In practice the orifice of the glass tube *a* is about 0·75 mm. bore, that of the hard-lead nozzle *d* is 4 mm. wide. In order to fix *a* in the hard-lead part *d*, the small india-rubber washer *b* is put on and placed with its orifice at the top, and *d* is put on with a twisting motion, but without exercising much pressure or trying to centre *a* exactly in *d*, the water pressure afterwards accomplishing this much better. With a pressure of 3 to 5 atmospheres and a properly adjusted nozzle no droplets whatever are formed, but a uniform mist travelling over a great distance. The Körting spray is bought in the ordinary way, and is fitted at the works with a glass jet, as shown here with every detail.

[Glass-nozzled spray-producers, precisely as here shown, have been employed for many years at one of the best conducted continental factories, and are still preferred there to every other form of apparatus of this kind. Since their introduction all previous trouble in feeding the chambers with liquid water has disappeared. The orifice of the glass jet has $\frac{3}{4}$ millim. bore, that of the hard-lead nozzle 4 millim. bore.]

A special advantage of the introduction of liquid water in the form of spray is that the temperature of the chambers is kept lower than when employing steam, since the latent heat of the latter, becoming free in its condensation, does not come into play. How useful such a cooling effect is, will be seen in Chapter VII. The only drawback to the spray system is the liability of the orifice of the spray-producer to get choked up by dirt, or else to be widened by corrosion. The former is avoided by careful filtration of the water, the latter by a suitable construction. Glass nozzles, as shown above, are much better even than platinum. I have found this system applied for many years with full succes-

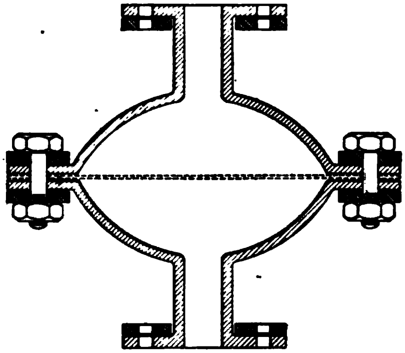
in a number of the best managed works, *e.g.* Griesheim and Aussig. Wherever it has proved unsuitable, this has been due to want of attention.

During the warmer portion of the year the whole of the chambers can be supplied with water as a spray; but in the winter season the back part of the system must sometimes get a little steam.

For all descriptions of spray-producers the water must be carefully filtered, preferably by means of sponge-filters. Benker moreover places wire-gauze in front of every spray-producer. He works these at a pressure of from 2½ to 5 atmospheres, by means of a small intermediate cylinder, about 3 feet wide and 6 or 9 feet high. For the first start a little high-pressure air is employed; afterwards the feed-pump gives sufficient pressure, which can be reduced by means of a tap if too much water is discharged.

This plan is very well illustrated by figs. 231 & 232 (folding plate), which at the same time show a chamber as erected by Mr. Benker for the French "high-pressure style." A is a small air-pump, B the water-pressure vessel, made ot an old steam-boiler, with two safety-valves, *a* and *b*. One of these, destined for the air, is very small; but the other, for the water, must be large enough to discharge the whole of the water supplied by pump D; otherwise B might burst. The second valve is weighted ½ atmosphere more than the air-valve. The level of the water in B must be kept 12 inches below the top. Pump D is an ordinary

Fig. 233.



feed-pump, kept continuously going; between B and D is interposed the sponge-filter C. The water rises in the high-pressure pipe EE to the top of the chamber, where there are taps *c c* at distances of about 16½ feet. Behind each tap is placed a leaden filter (shown on a larger scale in fig. 233), with a very fine wire-gauze sieve; then comes a swan-neck pipe, which passes through the chamber top, and this ends in a spray-producer, fig. 228 [or else 230]. From time to time the air-tap on B is opened in order to replace the air dissolved by the water under the high pressure.

Arrangements for producing the Draught in Vitriol-chambers.

The draught necessary for driving acid-chambers is produced by various agencies, the most important being the high temperature with which the gases leave the burners and enter the chambers, which counterbalances the greater density of the burner-gases when compared with that of air in the cold state. We shall calculate these factors for the various cases in question, employing the following values for the density of gases and vapours at 0° C. and 760 mm. mercurial pressure:—

	grams.
1 litre of dry atmospheric air weighs...	1·2932
1 ,, ,, oxygen	1·4298
1 ,, ,, nitrogen	1·2562
1 ,, ,, sulphur dioxide	3·8721
1 ,, aqueous vapour..................	0·804343

We shall begin with ***burner-gases from brimstone,*** the normal composition of which has been calculated (p. 397 *et seq.*) $=0{\cdot}1123\ SO_2+0{\cdot}0977\ O+0{\cdot}7900\ N=1$ litre of gas. This must weigh at 0° and 760 mm. pressure :

$$0{\cdot}1123\times2{\cdot}8731+0{\cdot}0977\times1{\cdot}4298+0{\cdot}7900\times1{\cdot}2562$$
$$=1{\cdot}4547 \text{ grams.}$$

Taking the temperature in the outlet-pipe from the brimstone-burner to average 100° C. (which is much below the actual temperature), the above 1·4547 grams would occupy a space of $\frac{273+100}{273}=1{\cdot}3663$ litres, or 1 litre of the burner-gas at 100° C. and 760 mm. $=\frac{1{\cdot}4547}{1{\cdot}3663}=1{\cdot}0647$ grams.

Atmospheric air at 0° and 760 mm. pressure weighs per litre 1·2932 grams; at 20° this quantity occupies the space of 1·0733 litres, at 35° = 1·1282 litres, so that even at the highest summer temperature, say 35° C., 1 litre of air weighs as much as $\frac{1 \cdot 2982}{1 \cdot 1282}$ = 1·1463 grams; it is therefore in any case heavier than the burner-gas at 100° C.

The aqueous vapour always present in the air need not be taken into account, since by its expansion in the heat of the burner it can only increase the difference between the weight of the gas and that of the air.

Owing to the fact that the gaseous mixture in the vertical pipe of the sulphur-burner is lighter than air, it must issue out of the top of the pipe into the chamber with a speed corresponding to the excess pressure of the atmosphere acting upon it from below. It must therefore by itself exercise a pressure upon the gas in the lead chamber. Its speed or the draught increases with the height of the vertical pipe; and the latter therefore ought to enter the chamber-side as high up as possible. By thus providing more than sufficient drawing-power the supply of air is assured in any case; and its excess can always be moderated by narrowing the area of the inlets.

A second cause of draught is the formation of sulphuric acid itself, as the space occupied by the consumed gas cannot remain empty, and must at once be filled again. The condensation of the gas to sulphuric acid thus acts as an aspirator.

A third cause of draught is the vertical pipe taking the gas away from the last lead chamber or the chimney with which it is connected. As the gas in these contains all the nitrogen introduced into the chambers with only 5 per cent. of oxygen (a mixture of 95 vols. N + 5 vols. O has the litre weight grav. 1·263; ordinary atmospheric air 1·293), as it is saturated with aqueous vapour, and as it is usually warmer and never can be colder than the atmospheric air, it must necessarily be lighter than the latter; this is evident without any calculation.

If the nitrogen-acids are not recovered by a special process, to be explained later on, the gas certainly contains a little of those acids and of sulphur-dioxide, by which its specific gravity is somewhat increased. We shall, however, see that their effect is very slight, and does not materially interfere with the causes producing the draught.

The draught produced by all the above-mentioned causes regulates the quantity of air which can enter the apparatus by openings of a certain size. We have already seen, on p. 397, that we must not introduce the exact quantity of air required for transforming the burnt sulphur into SO_3, but a certain excess, which we have calculated = 5·18 vols. of oxygen upon each 14 vols. of SO_2. With this, for each 14 vols. of SO_2,

$$\begin{array}{rrl} 14+7+5{\cdot}18=21+5{\cdot}18= & 26{\cdot}18 & \text{vols. oxygen,} \\ \text{and } 79+19{\cdot}50= & 98{\cdot}50 & \text{,, nitrogen,} \\ \hline \text{together} & 124{\cdot}68 & \text{,, atmospheric air,} \end{array}$$

must be introduced into the chambers. From this it follows that for each vol. SO_2 $\frac{124{\cdot}68}{14}=8{\cdot}906$ vols. of air are required. Now 1 litre of SO_2 at 0° and 760 millims. pressure weighs 2·8731 grams, and SO_2 consists of equal parts by weight of sulphur and oxygen. Accordingly 1 litre of SO_2 at 0° and 760 millims. contains

$$\begin{array}{l} \frac{2{\cdot}8731}{2}=1{\cdot}43655 \text{ gram sulphur,} \\ \text{and } 1{\cdot}43655 \text{ ,, oxygen.} \end{array}$$

Thus for each 1·43655 gram of sulphur burnt 8·906 litres air at 0° and 760 millims. are required. Since

$$1{\cdot}43655 : 1000 :: 8{\cdot}906 : x,$$

each 1000 grams or 1 kilogram sulphur requires $\frac{8906}{1{\cdot}43655}=6199$ litres air at 0° and 760 millims. pressure to be introduced into the sulphur-burner, weighing $6199 \times 1{\cdot}2932 = 8017$ grams or 8·017 kilograms.

At 20° C. this weight would occupy $\frac{273+20}{273} \times 6199 = 6653$ litres.

All these calculations refer to *dry* air. If the air is saturated with moisture, its volume is increased by the vapour-tension e for the temperature in question, according to the formula:

$$V^1 = \frac{V \times 760}{b-e},$$

where b is the actual barometric pressure. At 20° C., e is $= 17{\cdot}4$ mm., and for $b = 760$ the above 6653 litres will be = 6809 litres, if saturated with moisture.

The last increase of 156 litres is only fully realized in the exceptional case of air completely saturated with moisture. As this increase is only 2·34 per cent. of the volume of the necessary dry air, whilst, according to the calculation on p. 398, nearly 25 per cent. of the theoretical quantity of air (that is, more than ten times as much) is introduced in excess, the changes in the moisture of the air and the differences of volume resulting therefrom are of no practical consequence. We shall therefore not enter into a calculation of the differences caused by the real percentage of moisture in the air.

In the case of *pyrites-kiln gases*, it follows from the data given on p. 399, that for each 100 pts. of sulphur employed as FeS_2,

375 pts.	oxygen must be supplied for	oxidizing the Fe,
1000	,, ,, ,,	forming SO_2,
500	,, ,, ,,	oxidizing this to SO_3.

Since 1 litre of air at 0° and 760 millims. pressure weighs 1·4298 gram, at this temperature and pressure

375 grs.	O give	262·3 lit.	mixed in the air with	986·7 lit. N.
1000 ,,	,,	699·4	,, ,, ,,	2631·1 ,,
500 ,,	,,	349·7	,, ,, ,,	1315·5 ,,
1875 ,,	,,	1311·4	,, ,, ,,	4933·3

Theoretically, then, for each kilogram of sulphur consumed as FeS_2, $1311{\cdot}4 + 4933{\cdot}3 = 6244{\cdot}7$ litres air at 0° and 760 millims. pressure must be supplied.

The normal pyrites-burner gases, as calculated p. 400, contain 8·59 per cent. by vol. SO_2, 9·87 O, and 81·54 N (not reckoning any SO_3 present).

1 litre of this gas at 0° and 760 millims. weighs

$$0{\cdot}0859 \times 2{\cdot}8731 + 0{\cdot}0987 \times 1{\cdot}4298 + 0{\cdot}8154 \times 1{\cdot}2562 = 1{\cdot}4122 \text{ grm.}$$

whilst the 1 litre of the gas resulting from the combustion of brimstone, according to our former calculation, weighs 1·4547.

The former being, under equal conditions, lighter than the latter, consequently gives stronger draught.

Of course the volume of air necessary for a certain consumption of sulphur is also dependent upon the elevation of the site above the level of the sea, which regulates the mean barometrical pressure. Thus at Munich a quantity of air will occupy a space larger by 5·5 per cent. than the same quantity at Widnes or New York.

It is easy to introduce the minimum of air required for proper work. But this is not all; an excess of air is just as hurtful as a deficiency, although not to the same extent. Air in excess cools the gas, and thus may sometimes interfere with the process; it fills a portion of the chamber-space and renders it inoperative; it dilutes the gas and weakens the energy of the chemical action. The regulation of the supply of air must therefore be accurate, and must be adapted to the frequent variations in the state of the atmosphere. This must be done by great attention in enlarging or diminishing the openings serving for introducing the air and for taking away the gas. By either means the supply of air can be diminished; but it is not indifferent which of them is selected. By the latter the draught acting upon the contents of the chambers at the end of the apparatus, by the former the pressure upon the contents of the chambers at the beginning of the apparatus, is lessened. With the latter method the pressure inside the chambers is increased; with the former it is diminished. Accordingly, if the chimney-draught is too much cut off, the gas issues forcibly from any openings in the chambers, &c., whilst the air may enter properly by the holes in the front of the sulphur-burners. If, however, these latter are stopped up too far, the chambers suck in air in any places not completely closed against the atmosphere.

The draught may also be increased in two different ways, viz., by enlarging the opening in the exit-tube, or by increasing the inlet-holes in the door of the burner. Then the chambers, if the exit-tube is not sufficiently closed, suck in air; if, on the other hand, the inlet-openings are too wide, gas is forced out from any leaks in the chambers by the excess pressure. This is especially noticed when the doors are opened for charging. Both can be avoided by arranging a certain proportion between the inlet and the outlet openings. Usually the area of the latter is two-thirds that of the former. For the changes of draught made necessary by the variations in the state of the atmosphere no certain rules can be given; observation and practice must come into play here. In well-arranged works, however, this is not left to chance, but the supply of air is checked by regularly estimating the oxygen in the escaping gas, as we shall see later on.

We have thus seen that the hot gaseous mixture in itself contains the conditions for causing a draught, since it is much lighter than the air, and will always have a tendency to rise from the burners to the chambers. We must also point to the second source of draught, viz. the formation of liquid sulphuric acid within the chambers from the mixture of the gases, which must necessarily have an aspirating action, although not only from the burners, but from all sides.

Along with these two sources of draught furnished by the peculiar nature of the acid-making process itself, there must always be another arrangement for causing further draught, especially because otherwise the current of gas could not be turned into the required direction. In the simplest case a plain *outlet-pipe* behind or above the last chamber will suffice. The Belgian Commission of 1854 even preferred this arrangement to a chimney, because the latter might produce an excessive draught; and many factories work quite well in this way. But it cannot be said that the excessive draught of a chimney must lead to a loss of uncondensed gas and too quick a passage through the chambers; for it is always very easy to cut off an *excess* of draught by a damper &c. in the outlet; but it is nothing like so easy to increase the draught in the outlet-pipe or chimney if *insufficient*. For the latter object a *steam-injector* placed in the outlet-pipe was formerly considered the most convenient apparatus. Sometimes, in lieu of a proper injector, a simple steam-jet, turned in the direction of the draught, is used; but this is a very wasteful proceeding, and a proper Körting's injector, made of regulus metal (lead and antimony), should always be employed. Such injectors can be applied in various places. Scheurer-Kestner (Bull. Soc. Chem. xliv. p. 98) describes his experience in this direction. He employed a Körting's injector which produced a gaseous mixture of 7·9 per cent. steam and 92·1 per cent. air. Thus a quantity of 1814 kilog. of water in the shape of steam sufficed for aspirating the air required for burning 7000 kilog. of 45 per cent. pyrites. At first the injector was placed in the pipe entering into the first chamber. This is the best place, where there is no Glover tower, as the steam is then very serviceable for working the chambers, and thus costs nothing; but in case of a Glover tower this produces an excess of steam in the first chamber. The regulus metal of the injector wore out pretty quickly; nor could it be replaced by porcelain, which cracked very soon; a thin casing of platinum, however, was found sufficient for protecting a regulus injector. It was tried to place the injector between the first and second chambers, but here also too much steam was introduced into the chamber. This is avoided by applying the injector at the exit from the Gay-Lussac tower; but then all the steam is lost and the process is thus made expensive. In the case of seleniferous pyrites the injector between the burners and the chambers is stopped up so quickly with a deposit of selenium, that two injectors must be employed side by side, one of which can be cleaned out while the other one is going.

Steam-injectors between the Glover tower and the chambers are, as we see, impracticable. This holds good of any place in the system, except in the exit-pipe or chimney itself. But in the chimney where the steam cannot be utilized for the chamber process, they cause considerable expense.

It must not be overlooked that with steam-injectors a regulation is all the more called for, lest the draught should be too strong; and in the end a cheap source of draught, viz. the chimney, has been replaced by a dear one, without any gain as to constant supervision and regulation. We should accordingly in ordinary cases prefer a *chimney* to a steam-jet, all the more as the former will always be necessary in any case for the steam-boilers. Of course the chimney, to do its work, must be higher than the chambers.

Where a chimney cannot be employed for one reason or another, nothing remains but to have recourse to a mechanical contrivance (fan-blast), as will be described below.

It answers much the same purpose as a chimney if the outlet-pipe fixed to the last chamber has a considerable height—for instance, 50 feet (in the south of France). Where several sets of chambers exist in the same works, it is preferable to carry them all into a common chimney, providing the connecting-pipe of each set with a contrivance for regulating the draught. It is not a good plan to utilize for the chambers a chimney with which ordinary furnaces are connected, as the draught will be of a very variable character in this case, and the working of the chambers will not be easily kept entirely regular. Still, at some works this plan cannot be avoided, and must be provided for by more careful regulation of the draught. In such works more than anywhere else the automatically acting dampers, described below, are recommended to be used.

The employment of a chimney is even more advisable if, as is now the case in all well-appointed works, a Gay-Lussac tower is fixed at the end of the set. In this case the draught must be regulated with even greater care than otherwise; but there must be an excess of draught at disposal to begin with. It is also a great improvement if the "sight" necessary for checking the work of the tower (comp. Chap. VI.) can be arranged in the down-draught near the ground-level, or at least the gangway round the chambers. If there is no down-draught, but a direct top-draught out of the tower, it is always necessary to mount to the top to observe the "sight." It is certainly quite possible to employ the tower itself as a chimney, if it is built with its top a good deal higher than the chambers; and this is actually done at a good many works, but probably in some cases only because there is no chimney available. The drawbacks of this plan are well illustrated by the following passage from the official Alkali Reports, No. 21 (for 1884), p. 74:—"No. 2256. The vitriol-exit from the plant in which the pyrites smalls are burnt used to be at the top of the Gay-Lussac tower. I found an exceedingly high escape from here on my first three visits. The manager has since connected this exit to the main chimney, and now finds he can better regulate the draught in his chambers. Since this has been done the tests have been invariably good."

The more recent sets of chambers at Oker, utilizing the configuration of the ground, are arranged in such a way that the burners, Glover towers, chambers, and Gay-Lussac towers rise one above the other, terrace-wise. The outlet of the whole is at a height of 62 feet above the level of the burner-grates. Drawings of this arrangement are given by Bräuning (Preuss. Zeitschr. f. Berg-, Hütten- u. Salinenwesen, 1877, table ii.). It is stated there that formerly the draught could not be made sufficient, even by connecting the Gay-Lussac towers with the boiler-chimneys.

I have received the following notes concerning the Oker system during 1902:—A set of chambers, started in October 1883, was formerly connected by a 2-foot pipe from the Gay-Lussac towers with the steam-boiler chimney. The draught was good, but the chimney, made of common bricks, suffered very much. Since 1896, when the chimney became superfluous through the centralization of the boiler plant, the gases have been passed straight out of the Gay-Lussac tower in all five sets of chambers. The draught is quite sufficient, without any artificial help; but this is easy to understand from the conditions described above. There is also the convenience of running both the chamber-acid and the Gay-Lussac acid into the Glover tower by natural fall.

It has been noticed at Oker that a very long draught-pipe, connecting the last chamber with the tower, has the advantage of neutralizing to some extent the oscillations of the outer atmospheric pressure, and thus facilitating the regulation. Be this as it may, such a long pipe, although it causes some loss of draught by friction, will always be very useful, by cooling the gas previously to entering the absorbing-tower. The same has been found at the Stolberg works (1902).

Very frequently one chimney has to serve two or more sets of chambers. It is perfectly well understood, from innumerable analogous cases in ordinary firing operations, that, where several apparatus are served by the same chimney, special care must be taken that they receive the same amount of draught. Wherever possible, the main flues are taken separately to the chimney and are introduced into the latter in such a way as not to interfere one with another, which can be attained by erecting mid-feathers within the chimney. Where it is necessary to connect several sets of chambers with the same main flue, it must not be overlooked that the draught is stronger in the part nearer than in the part further removed from the chimney; by suitable arrangement of the dimensions, by avoiding sharp angles in the places where the branches form the main flue, by mid-feathers, and by regulation by means of dampers, a proper equalization can generally be attained.

Sometimes none of the ordinary measures secure an equal draught for two sets of chambers, even when the flues from these meet about the same distance from the chimney. In such cases it is best to make the individual flues end in a large chamber, from which starts the main leading to the chimney, and to fill this chamber loosely with bricks, of course not to such an extent that the draught is too much restricted. This produces numerous small and constantly changing currents, which prevent any one of the large currents getting the advantage of the others, and thus equalizes the draughts.

C. L. Vogt has patented (July 29th, 1875) a peculiar contrivance for producing draught in acid-chambers, which introduces the air along with the necessary steam through a pipe with an opening of $\frac{1}{4}$ inch. The steam is under a pressure of 3 to 4 atmospheres. Sorel ('Fabrication' &c. p. 291) states that this had been practiced in France 20 years earlier. Such a contrivance is only exceptionally called for; but there are cases in which a supply of air behind the burners seems desirable (7th Chapter).

At some factories they work in this way: the Glover tower is packed very loosely, and itself acts as a chimney, so that the burners have always very good draught and never blow out, whilst it is quite possible at the same time to keep the exit draught so low that there is some little outward pressure even in the last chamber. In the next Chapter we shall describe an arrangement by which this aim can be attained even more perfectly.

We have already said something about the principles according to which the supply of air must be regulated; and we shall have to return to this in the next Chapter. Here we can only remark that there must be in any case enough total draught *behind* the chambers, but not too much; otherwise, even if the burners themselves are protected against excess of draught by diminishing the air-holes below the grates, there is all the more tendency for air to enter the chambers from all other sides through the finest chinks and thus disturb the process. If the draught is excessive, the incubus of the vitriol-maker, pale chambers, at once makes its appearance.

Whether, therefore, the draught is produced by a chimney or by an open pipe, there must always be some contrivance *for regulating* it. At many works this is done by a simple damper, introduced into the respective lead pipe by a slit, luted with clay or not at all. The arrangement shown in fig. 234, partly in elevation, partly in section, and in fig. 235, in cross section, is far more perfect. The draught-pipe, *a a*, is widened out into a rectangular vessel surrounded by a jacket, *b b*, forming a hydraulic joint; and the damper, *c*, is surrounded on all sides by the jacket *d d*, dipping into the water-lute at *b*. The damper is raised and lowered by the help of the chain, pulley, and balance-weight, *e*, *f*, *g*.

In continental works the arrangement shown in fig. 236 is frequently met with. The draught-pipe, *a a*, is interrupted by a wider drum, *b*, divided into two parts by a horizontal diaphragm, *c*. The latter is perforated by a number of holes whose total area is

Fig. 234.

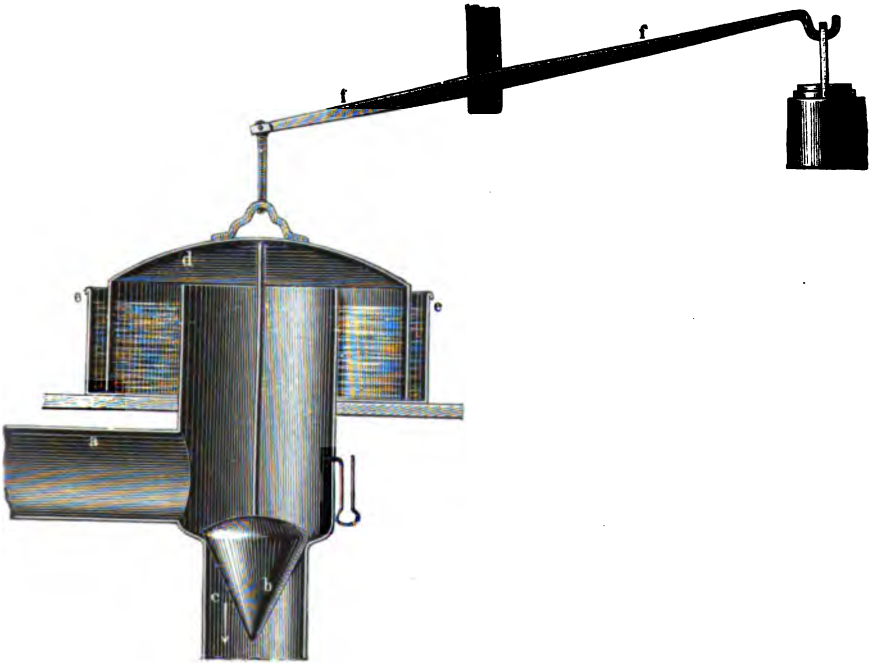
Fig. 235.

Fig. 236.

somewhat larger than that of the pipe, *a a*. When, therefore, *all* the holes are open, there is no obstacle whatever to the draught; but this can be produced at will by closing a certain number of the holes with clay or lead plugs. For this purpose the space above the diaphragm is accessible by a small door, which may consist of a pane of glass, *d* (fig. 236), to which another on the other side corresponds, so that the whole at the same time serves as a "sight."

Automatic regulation of the draught in the chambers.—Especially in the case of chambers not connected with a high chimney, where changes of wind &c. produce great variations of draught, it is advisable to adopt some automatic regulation along with the ordinary dampers, &c. Such an automatic apparatus can be made by putting on to the horizontal part of the exit-pipe a perpendicular 12-inch pipe, closed by a bell standing in an annular water-lute. The bell hangs on one arm of a lever, the other arm of which is so weighted that the bell can travel freely. When the draught is just right, this second arm has a certain position, in which a throttle-valve within the exit-pipe connected with it is half open. When the draught increases, the bell descends, owing to the increase of

Fig. 237.



atmospheric pressure, and partly shuts the throttle-valve; in the opposite case of the draught decreasing, the throttle-valve is opened wider. This apparatus, as constructed by M. Delplace, is shown in fig. 237, where *a* is the entrance-pipe from the Gay-Lussac tower, *c* the exit-pipe, *b* a conical valve, *d* the regulating bell, *e e* the water-line of the hydraulic joint, *f* the lever, *g* the balance-weight.

Somewhat different in detail, and apparently very accurately working, is the apparatus of Mr. W. G. Strype, of Wicklow, of which the following is a description (patent No. 705, Feb. 21st, 1879):—

The drawings illustrate two forms of the apparatus, fig. 238 being the most desirable, although somewhat more expensive in construction than the arrangement shown in fig. 239. Referring to fig. 238, an inverted vessel or receiver A, open at its lower end, dips into a tank A′, containing water or other suitable liquid acting as a hydraulic joint. The interior of A is placed in communication, by means of the pipe or passage *a b c*, with a receptacle R connected with the main flue from the Gay-Lussac towers and chambers. This receptacle is also in communication with a flue leading to the chimney, or other device for supporting the draught, and is divided by a partition having apertures fitted with valves or dampers D D, made of an alloy of lead and antimony. The operation of opening and closing D D to ensure uniformity of draught is regulated automatically by the action of the suction itself in the following manner:—The dampers are connected to a lever B, mounted and turning on a centre or fulcrum *e*. Suspended from one end of the lever is the vessel A, whilst the opposite end is loaded with a weight C, sufficient to preponderate to the required extent over the load of A. Assuming that the draught has an excess of "pull" over that which is adjusted and necessary for the proper working of the chambers, the dampers being open, the suction within the vessel A, when accelerated, will draw down that end of the lever and elevate the opposite or weighted end, and so partially close the dampers. C is so calculated that the weighted end of the lever can only be elevated when the required draught is exceeded, and it will fall by gravitation as soon as the draught is unduly diminished. It follows that thus the desired uniform action is obtained.

The connection between the dampers and the lever B is by means of rods or links passing through water-sealed stuffing-boxes, G G′; and to avoid friction these rods are suspended from knife-edge centres *d d′*. The other centres are constructed with knife-edges in like manner.

The vessel A becomes sensibly *lighter* when deeply immersed in the liquid, owing to the thickness of the sides, and would thereby constitute a source of disturbance to the proper action of the apparatus. To counteract this, the lever B is provided with a projecting arm E, carrying an adjustable weight F, arranged in such a position that, as the arm partakes of the motion of the lever, the centre of gravity of the system will be moved in the direction and to the extent necessary to effect the required correction.

Fig. 238.

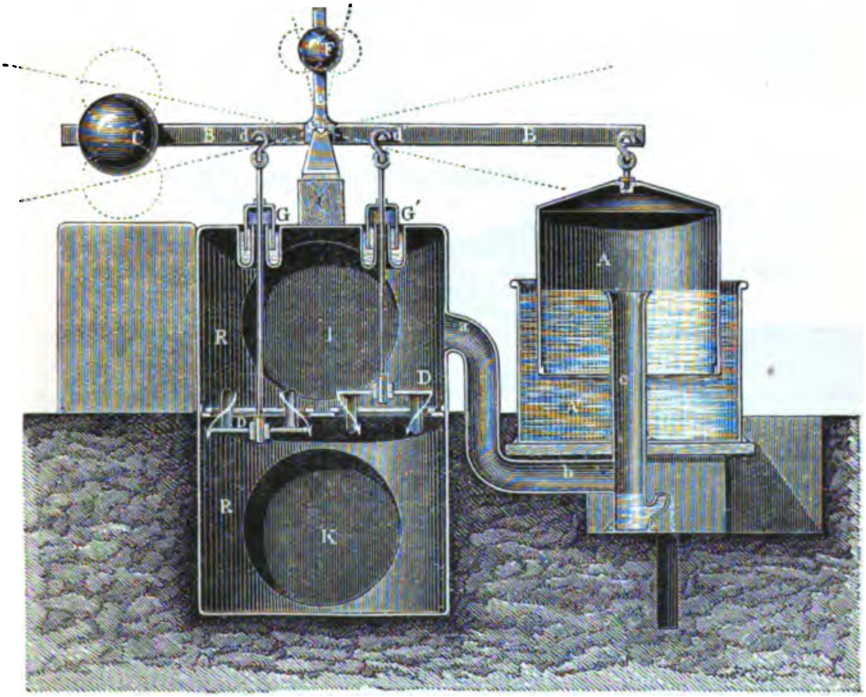
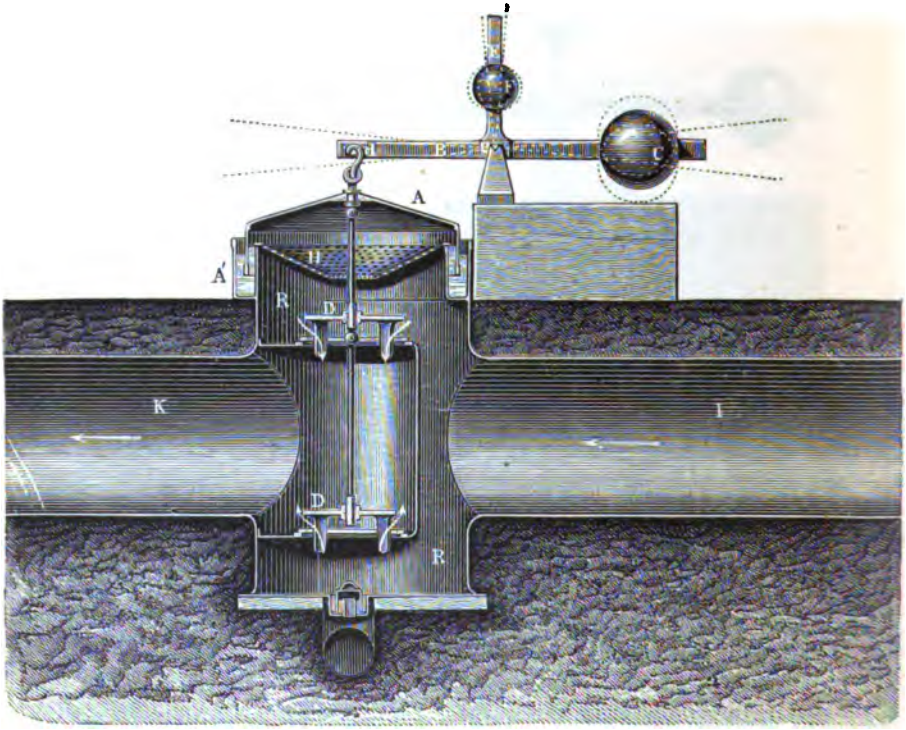


Fig. 239 is a simpler, and in some applications a more convenient form of the apparatus, the action being of course identical with that described for the arrangement in fig. 238. Should the draught fluctuate very much, the diaphragm shown dotted at H (with an opening in its centre to communicate with the vessel A) can be interposed to prevent the movements of the regulator being too sudden and rapid.

This apparatus has no wearing surfaces, is practically frictionless in its working, and is balanced in all positions. By means of it any disturbance to the steady and uniform flow of gases through the chambers caused by irregular chimney-draught is prevented, the admission of air to the burners is more uniform, the regulation of the proper quantity and relation of the gases to each other throughout the chambers is facilitated, and better working and more economical results are obtained in the process with less supervision and attention than hitherto required to carry on successfully the manufacture of sulphuric acid.

Fig. 239.



Mechanical Production of Draught in the Chamber System.

We have spoken above (p. 549) of the various drawbacks connected with the application of injectors for this object: I have indeed not found such apparatus at any of the works I have recently visited. But several works have adopted the plan, originally followed at Freiberg [*], of promoting the draught by fans made of lead alloyed with antimony, or wood or iron covered with lead, fixed on iron axles, running in somewhat tightly fitting lead journals without stuffing-boxes. Such fans are arranged either between the Glover tower and the first chamber, or between the last chamber and the Gay-Lussac tower, or in both places. These fans are worked at a trifling expense, most conveniently by electromotors, which avoid the necessity of shafting and gearing; and this process should be more frequently employed, not merely in such extreme cases as at the Freiberg works, where the gases must travel through flues of 330 feet length, but in ordinary chambers, which are thus made independent of accidental variations of pressure, of low chimneys, &c.

At the works of Messrs. Matthiesen and Hegeler at La Salle (Ill.), where zinc-blende is roasted in a mechanical shelf-burner, and the necessary draught for the chambers could not be obtained by a chimney, an iron fan-blast, covered with an alloy of lead and antimony, is placed between the Glover tower and the first chamber, and another such apparatus between the Gay-Lussac tower and the chimney. This arrangement had been working for several years when I visited the works in 1890.

The systematic production of draught by placing one fan behind the Glover tower and another in front of the Guy-Lussac has been especially worked out by F. J. Falding: comp. Min. Ind. vii. p. 672. In this way the draught of the burners is rendered independent of the pressure in the chambers, where quite different conditions prevail.

Falding's fans have a cast-iron casing lined with lead, and a spindle and arms made of antimony-lead. They are very carefully and substantially mounted, and work up to 700 revolutions per minute.

Niedenführ (1902) considers that a fan-blast would be best placed between the burners and the Glover tower, but he believes

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[*] According to Mühlhäuser (Zsch. angew. Ch. 1902, p. 672), this invention is due to a mining engineer of the name of Hagen, at the Halsbrücke works.

this to be impossible with ordinary fans on account of the high temperature and the flue-dust. Directly behind the Glover tower a fan would also act very well, but here antimony-lead is too quickly corroded, and it is therefore generally preferred to put the fan between the last chamber and the Gay-Lussac tower. Recently the firm of March Söhne, at Charlottenburg (now "Vereinigte Thonwaarenfabriken"), have constructed very good fans of stoneware, which probably will do perfectly well at temperatures below 70° C., for instance, between the Glover tower and the first chamber (comp. Chem. Zg. 1902, p. 1057). But even in that case it is best to place another fan between the last chamber and the Gay-Lussac tower. In very long sets with small sections, such as are found when a small original plant is gradually enlarged by adding more chambers, there is frequently irregular work with large consumption of nitre, which is very easily remedied by a rational use of fan-blasts.

Usually the fans are made of iron covered with lead, or altogether of "hard lead" or "regulus" (antimonial lead), but of course the axle or spindle should be made of iron, and the journals must also consist of this metal. This is a weak point, at least where there is heat to contend with as well as the acids. In very hot places, however, where lead is out of the question, cast-iron may be employed, which is not acted upon so long as no acid is condensed upon it. Here also the journals are the weak point, but this has been overcome by A. P. O'Brien, at Richmond, Va.; in the following manner (Falding, 'Min. Ind.' ix. p. 621):—A cast-iron fan is placed immediately behind the burners, before the nitre-oven and Glover tower. It serves five Herreshoff furnaces, consuming 30,000 lbs. 49 per cent. Rio Tinto fines per 24 hours. The fan has 27 in. suction and discharge, and is cast-iron throughout, including the spindle: it is covered with a 1-inch coat of asbestos cement. The temperature inside the fan is about 540° C. The journals are not oiled at all, but flooded with water from several ⅜-inch pipes. Water also surrounds the jacket of each journal, and is admitted to the oil-chamber in lieu of oil as a lubricant. After 9 months' work it had not required a cent's worth of repair or oil. No wrought-iron or steel is in contact with the gas, only cast-iron; otherwise there is nothing special in its construction.

Figs. 240 to 242 show the construction of a hard-lead fan, as constructed by H. Lentpold, at the Dora-Lys works at Pont Saint-Martin (communicated by him to the author). Fig. 240 is a sectional elevation, fig. 241 a sectional plan, fig. 242 a perspective view of the iron casing. It is clearly seen how the iron spindle is protected by a hard-lead casing.

Fig. 240.

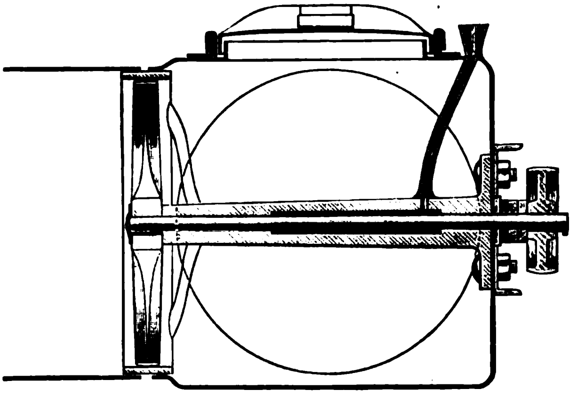
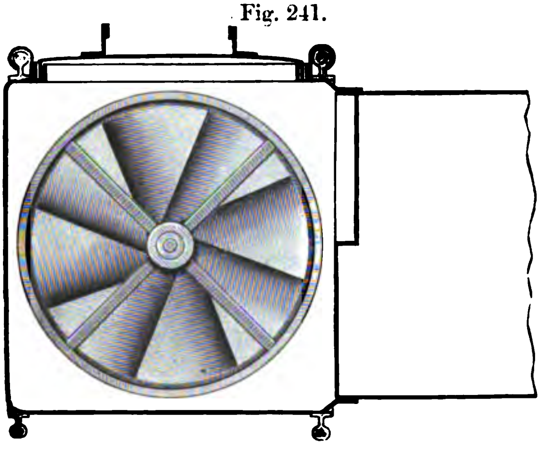


Fig. 241.



Benker (1902) always employs fan-blasts (and water-sprays) for the "high-pressure work" (comp. pp. 468, 543, and Chap. VII.), where 8 kil. acid of 116° Tw. is made per cubic metre in 24 hours. He places the fans preferably between two Gay-Lussac towers; if there is only one Gay-Lussac, the fan is placed behind this, but is followed by a small tower fed with water in order to condense the acid mist. For this purpose Benker prefers plate-towers to any other kind of apparatus; he places one of these towers at such a height that the weak acid contained therein can be run into the Glover tower. The object of the fan-blast is to avoid the inequalities and temporary losses of draught caused in the case of chimneys by wind, sunshine, &c., and to produce a regular composition of the exit-gases, 4·5 to 5 per cent. oxygen for ordinary pyrites, up to 6·5 per cent. for cupreous pyrites. As there is a difference of temperature between day and night, the speed of the fan must be regulated at least twice a day. Attempts at placing a fan between the Glover tower and the first chamber were not successful, principally on account of the necessity of frequent repairs, although even shells made of Volvic lava were tried.

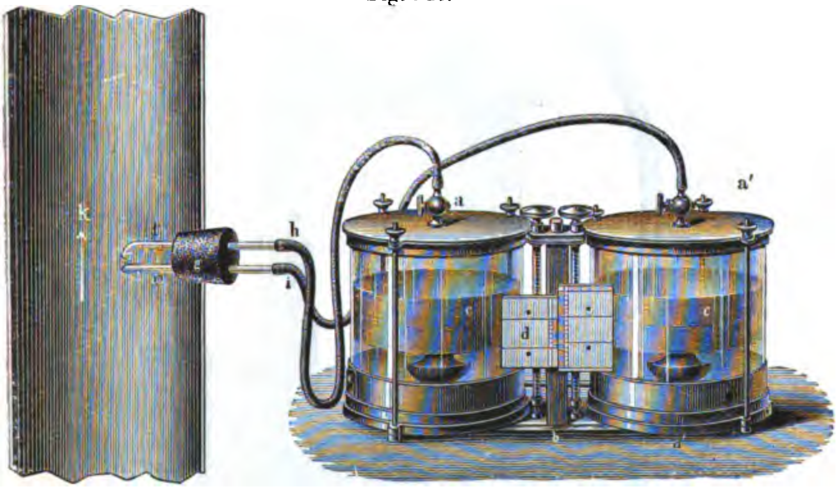
Fig. 242.

Anemometers.

Although we have in a previous Chapter (p. 322) excluded the use of a Combes' anemometer for regulating the access of air to the burners, because it is too delicate an instrument, and because it only shows the draught in the place which it occupies, we have here to speak of an anemometer adapted for controlling the draught. This is Péclet's *differential anemometer* as modified by Fletcher and Swan. Fletcher's modification is described in the Third

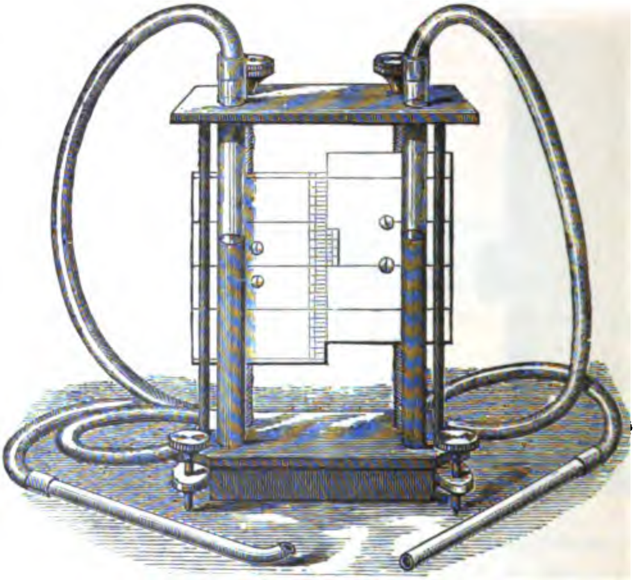
Annual Report on the Alkali Act, 1863, by the Inspector, for 1866, p. 54 *et seq.*; Swan's in the 'Transactions of the Newcastle Chemical Society,' Jan. 26, 1871. Péclet's anemometer is founded upon the physical principle that a current of air passing the open end of a tube causes a partial vacuum in the tube. If, therefore, a straight tube is introduced through a hole into a chimney, or into the draught-pipe taking away the chamber-gas, so that the gaseous current passes the open end of the tube at a right angle, a partial vacuum will be formed in the latter, proportionally to the velocity of the current; but the aspirating action of the chimney will be equally communicated to this tube. We must here distinguish between these two actions. To do this, we must introduce two tubes into the chimney, one of which ends straight, whilst the other is bent to a right angle, so that the current of air blows into it. Both tubes will now be affected by the aspirating action of the chimney; but in the straight tube this is *increased* by the aspirating action of the current crossing its open end, whilst in the bent tube it is dminished by the air blowing into it. The difference between the aspirating action of the two tubes is thus reducible to the action of the current of air; and by measuring it the speed of that current can be ascertained. For this purpose the two tubes are connected with a U-shaped glass tube containing water or another liquid; this will rise in one of the limbs to an extent corresponding to the difference

Fig. 243.



of suction. Since the sucking-action of the chimney acts upon both limbs, it is eliminated, and the difference of level corresponds merely to the different action exerted by the current of air upon the straight tube, which it crosses, and the bent one, into which it blows. This action rises and falls with the speed of the current; and the latter accordingly can be deduced from it. Water (used by Péclet), on account of the friction exercised in the U-tube, is only adapted for currents of a greater speed than 5 feet per second. Fletcher overcame this difficulty thus:—In order to lessen the friction, he employed two cylinders, *a a′* (fig. 243), of 4 inches diameter, connected at the bottom by a narrow tube, *b*. This arrangement is ten times as sensitive as a U-tube of 0·4 inch width would be, since the area upon which the pressure acts is increased 100-fold, but the circumference upon which friction acts only 10-fold. The rising and falling of the liquid is observed by means of metal floats, *c c*, upon which a very fine horizontal line is marked by a lathe; and the scale, *d*, provided with a vernier and a very fine adjusting-screw, permits the difference of level, down to one-thousandth part of an inch, to be read off. This is possible, not with water, whose mobility, owing to its adhesion to the glass,

Fig. 244.



is too slight, but with *ether*, whose adhesion is only one two-thousandth of that of water. The two glass tubes, *e* and *f*, are inserted into the draught-pipe, *k*, by means of a cork, *g*, at right angles to the current of gas (so that it blows into the bent tube, *f*), and are connected by elastic tubes, *h i*, with *a a′*.

The form of anemometer shown in fig. 243 has now been replaced by the simpler one represented in fig. 244. Lenses have also been added to make the readings more accurate; but these, in my experience, give more trouble in making the observations than is gained by the greater accuracy of reading the scales.

In the original communication by Mr. Fletcher, as well as in the first edition of this work (pp. 333–335), we find the mathematical evolution of the laws for ascertaining the relation of the readings to the speed of the currents. We abstain from repeating this reasoning here, and merely give the final formula found for ascertaining the velocity of the gaseous current *v* from the height of the column of ether (of 0·740 spec. gravity) $=p$, for any temperature *t* (in degrees Fahrenheit) and barometric pressure *h* (in inches) :—

$$v=\sqrt{p\frac{29{\cdot}92}{h}\times\frac{519}{459+t}}\times 28{\cdot}55.$$

The Table given on p. 567 *et seq.*, for the speeds corresponding to different readings of the anemometer, is computed from the formula

$$v=\sqrt{p}\times 28{\cdot}55\ ;$$

and another Table is added for correcting the variations in the temperature of the current of gas. The corrections for small variations in the barometrical pressure are usually not considerable; but they can be made by means of the above formulæ—

$$v''=\sqrt{p\frac{29{\cdot}92}{h}}\times 28{\cdot}55,$$

or

$$v=\sqrt{p\frac{h}{29{\cdot}92}}\times 28{\cdot}55.$$

If the pressure is read off in millimetres the number 760 is everywhere substituted for 29·92 ; or if the readings are in millimetres and the speed in metres per second is required to be known, the constant 28·55 is converted into another, according to the formula

$$\frac{0·3048}{\sqrt{25·4}} \times 28·55 = 1·727\ ;$$

so that the formula for v' and p' in metrical measures will read $v' = 1·727\ \sqrt{p'}$.

A correction for the expansion and contraction of the ether in the instrument itself is mostly unnecessary, since it is only exposed to the ordinary temperature; it amounts to about 1 per cent. of the speeds shown in the Table for each 10° F. ($=5°·55$ C.) deviation from 60° F.,—more for temperatures below, less for temperatures above 60° F.

In order to make the readings more exact, first the height of ether in one of the limbs is noticed, then the current is reversed by connecting the tube *e* with *a* and *f* with *a'* (fig. 243); another reading is made; and thus twice the difference of pressure caused by the suction at *f* is found. The number thus found is read off in Table I. and corrected for temperature by Table II. To take an instance, let the first reading be 1·039, and the second reading, after reversing the current, 0·861, the difference will be 0·178. On referring to Table I., the speed 12·05 feet per second will be found. This, however, is only true if the temperature of the air is 60° F. Should it in the case in question be 520° F., Table II. gives the correcting multiplier, 0·7280. This, multiplied by 12·05, is 8·772, the true speed of the current if measured at the temperature of 60° F.

This instrument is not influenced by soot, heat, or corrosive vapours; it can be placed at some distance from the flue to be tested, if longer elastic tubing be used; and it can, of course, be employed both for aspirating and for pressure currents (fan-blasts &c.), and as a measure for the speed of atmospheric currents.

Of course, like every other anemometer, Fletcher's only indicates the pressure at the place occupied by its receiving portion; and accordingly the tubes *e* and *f* must be introduced so far as to reach into the air-current to the extent of about one sixth of the diameter of the flue. The velocity at this place is assumed to be nearly equal to the average; but this is very doubtful, and there are no means at present known of measuring the absolute quantities of air passing through a flue of any considerable sectional area with any degree of certainty.

Table I.—*Showing the Speed of Currents of Air as indicated by the Ether Anemometer.*

$$v = \sqrt{p} \times 28{\cdot}55.$$

Temperature 60° Fahr. Barometer 29·29 inches.

Manometer reading.	Speed of air.	Manometer reading.	Speed of air.	Manometer reading.	Speed of air.
in.	ft. per sec.	in.	ft. per sec.	in.	ft. per sec.
0·001	0·903	0·047	6·189	0·093	8·707
0·002	1·277	0·048	6·255	0·094	8·754
0·003	1·564	0·049	6·320	0·095	8·800
0·004	1·806	0·050	6·384	0·096	8·846
0·005	2·019	0·051	6·448	0·097	8·892
0·006	2·212	0·052	6·510	0·098	8·938
0·007	2·389	0·053	6·572	0·099	8·983
0·008	2·554	0·054	6·634	0·100	9·028
0·009	2·709	0·055	6·695	0·102	9·118
0·010	2·855	0·056	6·756	0·104	9·207
0·011	2·994	0·057	6·816	0·106	9·295
0·012	3·127	0·058	6·876	0·108	9·383
0·013	3·255	0·059	6·935	0·110	9·469
0·014	3·378	0·060	6·993	0·112	9·554
0·015	3·497	0·061	7·051	0·114	9·639
0·016	3·612	0·062	7·109	0·116	9·724
0·017	3·723	0·063	7·166	0·118	9·808
0·018	3·830	0·064	7·223	0·120	9·891
0·019	3·935	0·065	7·279	0·122	9·972
0·020	4·038	0·066	7·335	0·124	10·053
0·021	4·137	0·067	7·390	0·126	10·13
0·022	4·235	0·068	7·445	0·128	10·21
0·023	4·330	0·069	7·500	0·130	10·29
0·024	4·423	0·070	7·554	0·132	10·37
0·025	4·514	0·071	7·608	0·134	10·45
0·026	4·604	0·072	7·661	0·136	10·53
0·027	4·691	0·073	7·713	0·138	10·60
0·028	4·777	0·074	7·766	0·140	10·68
0·029	4·862	0·075	7·819	0·142	10·76
0·030	4·945	0·076	7·871	0·144	10·83
0·031	5·027	0·077	7·922	0·146	10·91
0·032	5·107	0·078	7·974	0·148	10·98
0·033	5·187	0·079	8·025	0·150	11·06
0·034	5·265	0·080	8·075	0·152	11·13
0·035	5·342	0·081	8·125	0·154	11·20
0·036	5·418	0·082	8·175	0·156	11·27
0·037	5·492	0·083	8·225	0·158	11·34
0·038	5·565	0·084	8·275	0·160	11·42
0·039	5·638	0·085	8·324	0·162	11·49
0·040	5·710	0·086	8·373	0·164	11·56
0·041	5·781	0·087	8·421	0·166	11·63
0·042	5·851	0·088	8·469	0·168	11·70
0·043	5·921	0·089	8·517	0·170	11·77
0·044	5·989	0·090	8·565	0·172	11·84
0·045	6·056	0·091	8·613	0·174	11·91
0·046	6·123	0·092	8·660	0·176	11·98

TABLE I. (continued).

Manometer reading.	Speed of air.	Manometer reading.	Speed of air.	Manometer reading.	Speed of air.
in.	ft. per sec.	in.	ft. per sec.	in.	ft. per sec.
0·178	12·05	0·284	15·23	0·390	17·83
0·180	12·11	0·286	15·28	0·392	17·88
0·182	12·18	0·288	15·33	0·394	17·93
0·184	12·25	0·290	15·38	0·396	17·98
0·186	12·31	0·292	15·44	0·398	18·02
0·188	12·38	0·294	15·49	0·400	18·06
0·190	12·45	0·296	15·54	0·402	18·11
0·192	12·51	0·298	15·59	0·404	18·16
0·194	12·57	0·300	15·64	0·406	18·20
0·196	12·64	0·302	15·70	0·408	18·24
0·198	12·71	0·304	15·75	0·410	18·28
0·200	12·77	0·306	15·80	0·412	18·33
0·202	12·83	0·308	15·85	0·414	18·38
0·204	12·90	0·310	15·90	0·416	18·42
0·206	12·96	0·312	15·95	0·418	18·46
0·208	13·02	0·314	16·00	0·420	18·50
0·210	13·08	0·316	16·05	0·422	18·55
0·212	13·15	0·318	16·10	0·424	18·60
0·214	13·21	0·320	16·15	0·426	18·64
0·216	13·27	0·322	16·20	0·428	18·68
0·218	13·33	0·324	16·25	0·430	18·72
0·220	13·39	0·326	16·30	0·432	18·77
0·222	13·45	0·328	16·35	0·434	18·82
0·224	13·51	0·330	16·40	0·436	18·86
0·226	13·57	0·332	16·45	0·438	18·90
0·228	13·63	0·334	16·50	0·440	18·94
0·230	13·70	0·336	16·55	0·442	18·99
0·202	13·76	0·338	16·60	0·444	19·03
0·234	13·82	0·340	16·65	0·446	19·07
0·236	13·88	0·342	16·70	0·448	19·11
0·238	13·94	0·344	16·75	0·450	19·15
0·240	13·99	0·346	16·80	0·452	19·20
0·242	14·05	0·348	16·85	0·454	19·24
0·244	14·11	0·350	16·89	0·456	19·28
0·246	14·17	0·352	16·94	0·458	19·32
0·248	14·23	0·354	16·99	0·460	19·36
0·250	14·28	0·356	17·04	0·462	19·41
0·252	14·34	0·358	17·09	0·464	19·45
0·254	14·40	0·360	17·13	0·466	19·49
0·256	14·45	0·362	17·18	0·468	19·53
0·258	14·50	0·364	17·23	0·470	19·57
0·260	14·56	0·366	17·28	0·472	19·62
0·262	14·62	0·368	17·33	0·474	19·66
0·264	14·68	0·370	17·37	0·476	19·70
0·266	14·74	0·372	17·42	0·478	19·74
0·268	14·79	0·374	17·47	0·480	19·78
0·270	14·84	0·376	17·52	0·482	19·82
0·272	14·90	0·378	17·56	0·484	19·86
0·274	14·96	0·380	17·60	0·486	19·90
0·276	15·01	0·382	17·65	0·488	19·94
0·278	15·06	0·384	17·70	0·490	19·98
0·280	15·11	0·386	17·75	0·492	20·02
0·282	15·17	0·388	17·79	0·494	20·06

TABLE I. (continued).

Manometer reading.	Speed of air.	Manometer reading.	Speed of air.	Manometer reading.	Speed of air.
in.	ft. per sec.	in.	ft. per sec.	in.	ft. per sec.
0·496	20·10	0·590	21·94	0·700	23·89
0·498	20·14	0·600	22·12	0·750	24·73
0·500	20·18	0·610	22·30	0·800	25·54
0·510	20·38	0·620	22·48	0·850	26·32
0·520	20·58	0·630	22·66	0·900	27·08
0·530	20·78	0·640	22·84	0·950	27·83
0·540	20·98	0·650	23·02	1·000	28·55
0·550	21·17	0·660	23·20	1·250	31·93
0·560	21·37	0·670	23·38	1·500	34·97
0·570	21·56	0·680	23·55	1·750	37·77
0·580	21·75	0·690	23·72	2·000	40·37

TABLE II.—*Showing the Values of* $\sqrt{\frac{519}{459+t}}$ *for Values of t from* 0 *to* 1000; *or Corrections for Temperature.*

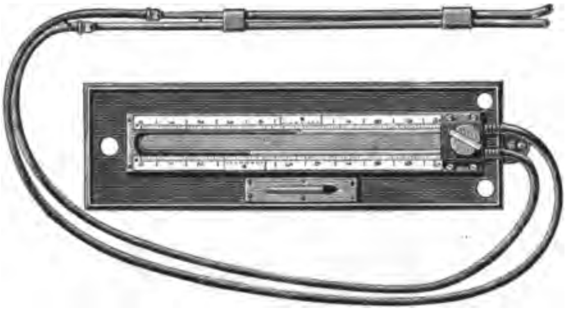
t, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$.	*t*, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$.	*t*, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$.
0	1·0634	130	0·9388	260	0·8497
5	1·0577	135	0·9348	265	0·8467
10	1·0520	140	0·9309	270	0·8438
15	1·0464	145	0·9270	275	0·8409
20	1·0409	150	0·9232	280	0·8380
25	1·0355	155	0·9194	285	0·8352
30	1·0302	160	0·9156	290	0·8324
35	1·0250	165	0·9119	295	0·8296
40	1·0198	170	0·9083	300	0·8269
45	1·0148	175	0·9047	305	0·8242
50	1·0098	180	0·9012	310	0·8215
55	1·0049	185	0·8977	315	0·8189
60	1·0000	190	0·8943	320	0·8163
65	0·9952	195	0·8909	325	0·8137
70	0·9905	200	0·8875	330	0·8111
75	0·9858	205	0·8841	335	0·8085
80	0·9812	210	0·8808	340	0·8060
85	0·9767	215	0·8775	345	0·8035
90	0·9723	220	0·8743	350	0·8010
95	0·9679	225	0·8711	355	0·7985
100	0·9636	230	0·8680	360	0·7960
105	0·9593	235	0·8649	365	0·7936
110	0·9551	240	0·8618	370	0·7912
115	0·9509	245	0·8587	375	0·7888
120	0·9468	250	0·8557	380	0·7865
125	0·9428	255	0·8527	385	0·7842

TABLE II. (continued).

t, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$.	t, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$.	t, degrees Fahrenheit.	$\sqrt{\frac{519}{459+t}}$.
390	0·7819	595	0·7017	800	0·6420
395	0·7786	600	0·7000	805	0·6407
400	0·7763	605	0·6983	810	0·6395
405	0·7741	610	0·6967	815	0·6382
410	0·7729	615	0·6951	820	0·6369
415	0·7707	620	0·6935	825	0·6357
420	0·7685	625	0·6919	830	0·6345
425	0·7663	630	0·6903	835	0·6333
430	0·7641	635	0·6887	840	0·6321
435	0·7619	640	0·6871	845	0·6309
440	0·7598	645	0·6856	850	0·6297
445	0·7577	650	0·6841	855	0·6285
450	0·7556	655	0·6826	860	0·6273
455	0·7535	660	0·6811	865	0·6261
460	0·7514	665	0·6796	870	0·6249
465	0·7494	670	0·6781	875	0·6237
470	0·7474	675	0·6766	880	0·6225
475	0·7454	680	0·6751	885	0·6214
480	0·7434	685	0·6736	890	0·6203
485	0·7414	690	0·6721	895	0·6192
490	0·7394	695	0·6706	900	0·6181
495	0·7375	700	0·6691	905	0·6169
500	0·7356	705	0·6676	910	0·6158
505	0·7337	710	0·6662	915	0·6147
510	0·7318	715	0·6648	920	0·6136
515	0·7299	720	0·6634	925	0·6125
520	0·7280	725	0·6620	930	0·6114
525	0·7261	730	0·6606	935	0·6103
530	0·7243	735	0·6592	940	0·6092
535	0·7225	740	0·6578	945	0·6081
540	0·7207	745	0·6565	950	0·6070
545	0·7189	750	0·6552	955	0·6059
550	0·7171	755	0·6538	960	0·6048
555	0·7153	760	0·6524	965	0·6037
560	0·7137	765	0·6511	970	0·6026
565	0·7119	770	0·6498	975	0·6015
570	0·7102	775	0·6485	980	0·6004
575	0·7085	780	0·6472	985	0·5994
580	0·7068	785	0·6459	990	0·5984
585	0·7051	790	0·6446	995	0·5974
590	0·7034	795	0·6433	1000	0·5964

Fletcher's anemometer has been improved by Swan in the following way, practically returning to Péclet's original construction (a similar plan has been independently proposed by P. Hart, Chem. News, vol. xxi. p. 200). In lieu of the 4-inch cylinders he takes a U-tube of $\frac{1}{8}$ inch diameter, narrowed in the bend to diminish the oscillations. The tube is 10 inches long, and placed with an inclination of 1 in 10; each limb has a scale and vernier, the latter partly made of glass and covering at the same time the scale and the tube, so that it is easy to read off to $\frac{1}{100}$ inch. The ends of the tube are connected with a two-way cock, so that the current can be reversed without opening any joint. Fig. 245 shows the instrument as seen from above, so that its inclination to the vertical line does not appear. It is fixed on a stand provided with a spirit-level and adjusting-screws. It is employed just like Fletcher's anemometer; but, owing to the inclination of 1 in 10, the column of ether in the tube occupies ten times the space corresponding to its height, and the reading of $\frac{1}{100}$ inch gives thus the same result as the very difficult one to $\frac{1}{1000}$ inch in Fletcher's instrument. The narrowness of the tubes does not matter in the case of ether, as the friction may be entirely neglected with this substance (the later form of Fletcher's anemometer, shown in fig. 244, bears this out as well). Swan's anemometer must always be placed exactly level in the direction of its length; but it need not be levelled across, if a reading be made in one limb, the two-way cock turned, and the new reading in the same limb subtracted from the first; thus it is unnecessary to read off at both limbs, which would involve levelling across as well. The speeds are found from Fletcher's table, dividing the readings by 10. Quite similar to the above is the pressure-guage designed by Sorel (comp. *suprà*, p. 509).

Fig. 245.

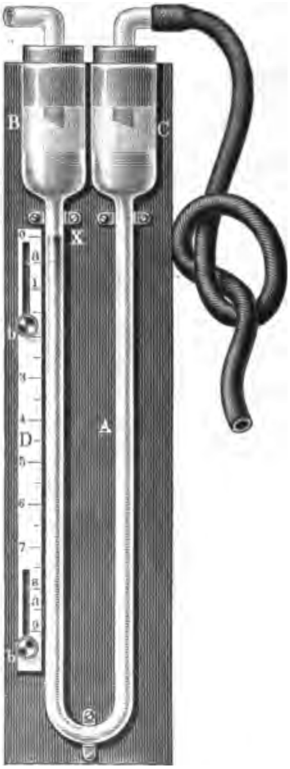


Other instruments for measuring the draught are, for instance, those of Kretz (Dingl. Journ. cxc. p. 16), of Ramsbottom (ib. clxxx. p. 334), of Scheurer-Kestner (ib. ccvi. p. 448 and ccxxi. p. 427), none of which can vie with Fletcher's in sensitiveness.

The very ingenious anemometer of Hurter (Dingl. Journ. ccxxix. p. 160) is only adapted for laboratory use. Compare also Bourdon's multiplying anemometer (Compt. Rend. vol. xciv. p. 5; Journ. Soc. Chem. Ind. 1882, p. 60).

One of the most delicate anemometers is Fryer's, described in the Inspector's Report on the Alkali Acts for 1877–78, p. 68. Its principle is to measure the difference of pressure on each side of a watch-glass shaped copper plate connected with a spiral spring. It will measure a pressure of $\frac{1}{3000}$ of an inch.

Fig. 246.



Recently differential anemometers on another principle have come into use very largely, and seem to be preferable to all others. There are already a good many forms of this apparatus, one of the best known being that of Professor Seger (G. P. 19,426), shown in fig. 246. The calibrated U-tube A is surmounted by two cylindrical cups, B and C, of equal width. The board on which it is fastened also carries the sliding-scale D, adjustable by slits *a a* and screw-pins *b b*. The tube is filled with two not miscible liquids, for instance heavy paraffin oil and dilute, coloured spirits of wine, of nearly equal specific gravity, to such an extent that the zero-point of the scale D can be put exactly at the line of contact of both liquids at X. If an aspirating force is acting on the surface of the liquid in C, which raises the level in that part of the tube, the point X will be lowered at a multiplied ratio, corresponding to the difference in the sectional area of the narrow part of A and the enlargement in C. If, for instance, the ratio of the sections is as 1 to 20, a difference of pressure of 1 millimetre will be indicated on the scale by a sinking of X to the amount of 20 millimetres. The scale is graduated in such a way that it indicates the pressure, expressed in millimetres of water. This instrument is much cheaper and easier to handle than those constructed on Péclet's principle and quite as accurate.

Calculation of the Volume of Chamber-gases according to Temperature and Moisture.

In all calculations concerning chamber-gases it is not sufficient to take into account the difference of temperature and barometric pressure from the normal state of 0° and 760 millim., but the amount of moisture present in the chamber-atmosphere must be equally brought into the calculations. It is evidently impossible to do this on the assumption that the tension of aqueous vapour within the chambers is that ordinarily existing for any given temperature; the presence of sulphuric acid, not merely at the bottom but all over in the shape of mist, greatly changes the aqueous-vapour tension according to the varying strength of the acid. The tables of Regnault and Sorel, given on pp. 195 and 196, would admit of making the calculation in the proper manner; but it will be more convenient to consult the following Table, p. 574 (calculated by Sorel), which immediately gives the *volume occupied by a cubic metre* (or cubic foot) *of air, originally at* 0° *C. and* 760 *millimetres pressure, after being brought into equilibrium of temperature and vapour-tension with dilute sulphuric acid of varying strength and temperature,* but without any change of pressure.

Percentage of H_2SO_4 in the acid.	10°.	15°.	20°.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°.	65°.	70°.	75°.	80°.	85°.	90°.	95°.
44	1·042	1·063	1·085	1·108	1·133	1·160	1·192	1·225	1·263									
46	1·042	1·062	1·084	1·107	1·131	1·157	1·188	1·218	1·256	1·303	1·356	1·427						
48	1·042	1·062	1·083	1·105	1·129	1·155	1·185	1·212	1·249	1·292	1·341	1·397	1·478	1·542				
50	1·041	1·061	1·082	1·104	1·128	1·152	1·180	1·207	1·241	1·281	1·327	1·377	1·452	1·509	1·589	1·756	1·911	
52	1·041	1·060	1·081	1·103	1·125	1·150	1·177	1·202	1·234	1·270	1·313	1·359	1·429	1·478	1·562	1·662	1·830	2·014
54	1·040	1·060	1·080	1·102	1·122	1·147	1·175	1·198	1·227	1·260	1·301	1·343	1·408	1·449	1·526	1·625	1·752	1·904
56	1·040	1·059	1·079	1·100	1·121	1·144	1·169	1·194	1·222	1·252	1·290	1·328	1·388	1·423	1·490	1·589	1·684	1·813
58	1·039	1·059	1·078	1·099	1·120	1·142	1·166	1·190	1·215	1·244	1·279	1·313	1·369	1·400	1·456	1·534	1·625	1·734
60	1·039	1·058	1·077	1·098	1·119	1·140	1·163	1·186	1·209	1·237	1·260	1·299	1·352	1·368	1·428	1·495	1·575	1·668
62	1·038	1·058	1·077	1·097	1·118	1·138	1·160	1·182	1·204	1·230	1·261	1·289	1·335	1·357	1·402	1·462	1·532	1·613
64	1·038	1·057	1·076	1·096	1·117	1·136	1·158	1·178	1·200	1·224	1·253	1·279	1·322	1·337	1·379	1·431	1·493	1·562
66	1·038	1·057	1·076	1·095	1·116	1·135	1·157	1·175	1·197	1·219	1·246	1·271	1·311	1·324	1·362	1·408	1·464	1·522
68	1·038	1·056	1·075	1·095	1·114	1·134	1·156	1·173	1·194	1·215	1·239	1·263	1·302	1·316	1·347	1·388	1·437	1·488
70	1·038	1·056	1·075	1·094	1·114	1·133	1·155	1·172	1·192	1·212	1·235	1·258	1·293	1·308	1·338	1·366	1·412	1·456
72	1·038	1·056	1·074	1·094	1·113	1·132	1·153	1·171	1·191	1·210	1·232	1·254	1·289	1·302	1·330	1·344	1·391	1·429
74	1·037	1·056	1·074	1·093	1·112	1·131	1·152	1·170	1·190	1·209	1·229	1·251	1·284	1·296	1·321	1·340	1·374	1·407
76	1·037	1·055	1·074	1·093	1·111	1·131	1·151	1·169	1·189	1·208	1·227	1·248	1·280	1·291	1·313	1·337	1·362	1·388
78	1·037	1·055	1·074	1·092	1·111	1·130	1·150	1·168	1·188	1·207	1·226	1·246	1·277	1·287	1·307	1·330	1·352	1·376
80	1·037	1·055	1·073	1·092	1·110	1·130	1·149	1·167	1·187	1·206	1·225	1·245	1·275	1·284	1·303	1·324	1·345	1·367
82	1·037	1·055	1·073	1·091	1·110	1·129	1·149	1·166	1·186	1·205	1·224	1·244	1·274	1·282	1·300	1·318	1·339	1·359