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TECHNICAL GAS-ANALYSIS

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BY

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PREFACE

In 1885 the Author published an English translation of Clemens Winkler's *Anleitung zur chemischen Untersuchung der Industrie-Gase*, under the title: *Handbook of Technical Gas Analysis*, and in 1902 a second edition of that book. In both cases he had made a few remarks and additions of his own, but in the main the book was, what it purported to be, a translation of the book of his friend, Professor Winkler, who died in 1904.

During the twelve years succeeding the second edition of the *Handbook*, the methods of Technical Gas-Analysis have been the subject of numerous investigations and publications which have brought about very important changes in that branch of chemical science. When, therefore, the time had come for issuing a new edition, the Author decided not to go over the old ground again, but to start on a fresh basis, and to describe the methods of Technical Gas-Analysis in his own way, using Winkler's book merely as one of various sources, apart from his own investigations. The result was the composition of this present treatise, which the Author has tried to make as comprehensive and generally useful as possible, without attempting to mention everything published on the subject in question—a course which would have unduly swelled the size of the volume, without corresponding benefit to the reader. He hopes that his effort may be appreciated as successful by the chemists working on Gas-Analysis.

G. LUNGE.

ZÜRICH, *July* 1914.

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TECHNICAL GAS-ANALYSIS

GENERAL REMARKS ON TECHNICAL GAS-ANALYSIS.

THE scope of technical gas-analysis naturally differs from that of gas-analysis for scientific purposes, as we need not explain in detail. We will only point out that technical gas-analysis is principally carried out in two directions: firstly, for the checking and regulation of many industrial operations, by which solid, liquid, or gaseous products are obtained; secondly, for the examination of gases prepared on a large scale as final products for various purposes.

Especially in the first case there is mostly no necessity of attaining the same degree of accuracy as is justly demanded for scientific purposes. Even if such accuracy could be attained, it would not, for the practical purpose in question, (that is, for the checking of industrial operations), in most cases possess any greater value than merely approximate estimations which can be made by the expenditure of much less time, with simpler apparatus and by less skilled persons. On the contrary, it is usually infinitely more important to carry out the analytical processes in as short a time as possible, in order to employ the result for regulating the technical operation accordingly. Even if a whole host of highly trained scientific chemists were at disposal (which, of course, is practically impossible), their results would come in too late and be useless to the technical manager, who mostly learns all he requires for his purposes by rapid and frequent tests, often carried out by merely empirically trained persons.

There are certainly cases where even for the manufacture of commercial products the greatest obtainable degree of accuracy in testing for impurities is required, and here all the best methods known must be employed. Frequently special methods have been developed, in which the fullest accuracy is combined with the possibility of reaching this in a short time. These exceptional cases will be dealt with, of course, in this treatise. Apart from these we claim for the methods of *technical* gas-analysis, as for technical analysis generally, that they should be carried out in the least possible time, at that degree of accuracy which is required for their specific purpose. Just on this account frequently special apparatus are employed in technical laboratories, which we do not find in scientific laboratories where time is no object.

Whether the analysis of gases be effected for scientific or for technical purposes, it is only exceptionally performed by gravimetrical methods, but mostly volumetrically, and the results are consequently in most cases not stated in per cent. by weight, but by volume. In those cases where gravimetrical methods are employed in this field, the weights found are reduced to volumes, for which purpose a number of tables will be found in this treatise. The volume of the gases is always calculated for "normal" conditions of temperature, atmospheric pressure and moisture, viz., for a temperature of 0°, a pressure of 760 mm., and the perfectly dry state. In "technical" gas-analysis this correction may be sometimes omitted in such cases where the analyses do not require any considerable degree of accuracy, and where the saving of *time* is an object. For the purpose of carrying out technical processes, very accurate results, which can be obtained only in the course of many hours or even of several days, as is sometimes the case, are useless for the management of the works, and the employment of such methods must be restricted to scientific investigations.

Burrell and Seibert (*8th Intern. Cong. Appl. Chem. Appendix*, xxv. p. 189) contend that the ordinary way of calculating the results of gas-analysis is not correct, since it rests on the assumption that the molecular volumes of all gases are alike, which, according to them, is not the case. However that may be, *technical* gas-analysis will not be affected by it.

The analytical processes employed in gas-analysis belong principally to the following classes:—

1st. *Absorption* of the constituent sought for from the gaseous mixture by a liquid or solid reagent, and measuring the reduction of volume thereby effected.

2nd. *Combustion* of one or more of the constituents, after addition of oxygen or of an oxygen-producing substance, and measuring the contraction thereby effected, sometimes after removing one or more of the products of combustion by absorbing reagents.

3rd. *Titration* of the constituent sought for in the manner so frequently employed in both scientific and technical analysis.

4th. *Gravimetrical* estimations of a gaseous constituent by absorbing it in a substance with which it forms a compound capable of being weighed.

SAMPLING.

For all practical purposes it is just as important that the samples of the gas to be analysed should be taken in the proper manner, as that the analysis itself should be carried out correctly.

In very many cases the composition of the gases to be analysed varies very much during the manufacturing process. To give a special instance :—

Fire-gases (chimney-gases) from steam boilers showed in a practical case :—

	1 minute after putting on fresh coal.	12 minutes later.
Carbon dioxide	13·5 per cent.	4·0 per cent.
Carbon monoxide	0·0 ,,	0·0 ,,
Oxygen	5·5 ,,	16·5 ,,
Nitrogen	81·0 ,,	79·5 ,,
Smoky particles	present	absent

In all such cases the analysis of a single sample rarely possesses any value. But even the continuous drawing off a sample of the gases (for which purpose Huntly, in *J. Soc. Chem. Ind.*, 1910, p. 512, and Gray, *ibid.*, 1913, p. 1092, describe suitable apparatus, *v. infrà*) rarely represents a real average of their composition. A truly reliable judgment on the process going on in the fireplace can be only obtained by a number of single tests, taken rapidly after one another, by which the influence of the stoking, etc., can be ascertained.

Of great importance is also the *place* at which the sample is taken. Thus, for instance, it is not advisable to test fire-gases by samples taken out of the chimney, where they are too much liable to be diluted by air drawn in; the sample should be taken out of the flue leading the gases to the chimney, as near as possible to the furnace.

In the case of gas-conduits of somewhat considerable dimensions, the composition of a gaseous mixture frequently varies at different places. The sample tube inserted in the gas main should therefore extend through the pipe or channel from side to side, and should have a fine longitudinal exit, or a series of small holes all along, so as to guarantee as much as possible the average composition of the gas.

Winkler recommends aspirating a strong current of gas, and employing for analysis a small side-current, by means of a T-pipe.

Before collecting the gas, the *air* must be completely removed from the connecting tubes and other intermediary apparatus, which is best done by interposing in the connecting tube immediately before its junction with the collecting vessel, a T-shaped branch provided with a tap. If the gas is under pressure, it is allowed to issue from that side-branch for some little time before closing the tap; if there is no pressure, the side-branch is connected with a small india-rubber aspirating pump, by means of which the air is removed between the place whence the sample is taken and the tubing filled with the gas to be analysed.

The *aspirating pipes* must, at the temperature to which they are exposed, be capable of resisting both the heat and the chemical action of the gases.

India-rubber tubes must therefore not be employed, except in short pieces for connecting tubes of other material, the ends of which are brought closely together. Even thick-walled rubber tubes allow the passage of small quantities of gas, but they are very much improved by painting with copal varnish (Lunge and Harbeck, *Z. anorg. Chem.*, xvi. p. 30).

Wherever possible, *glass* tubes are employed, which are chemically indifferent and easy to clean.

For taking samples out of spaces where glass would soften or fuse, *porcelain* tubes are usually employed of such length that the gases are sufficiently cooled down before they are conveyed further on in glass tubes. Porcelain tubes are liable to crack if they are suddenly exposed to high temperatures, and they must therefore be carefully heated up before putting them in. *Quartz* tubes are not exposed to cracking, but they can be employed only up to 1000°; above this they are not gas-tight. Unglazed earthenware tubes are of course much too porous for this purpose.

The aspirating tubes are put in a suitable hole in the place from which the samples are to be taken. In many cases they may be fixed there by means of a cork, or an india-rubber stopper, *e.g.* in the side of a vitriol-chamber, or in other places where the temperature admits of it. Where it is possible, a special short side-tube is put in the apparatus for that purpose.

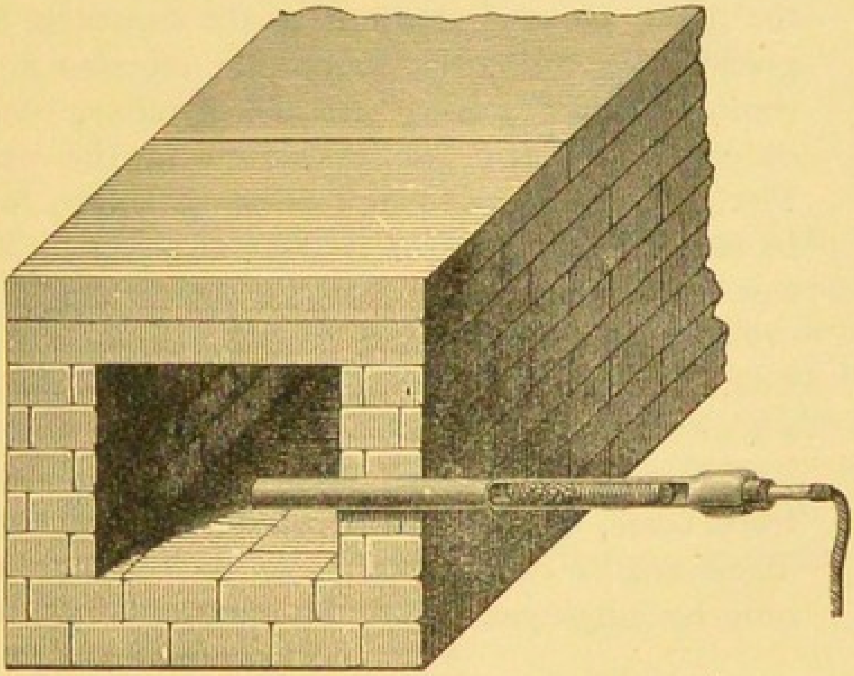

FIG. 1.

In other cases, especially where masonry has to be penetrated (*e.g.* in gas-producers or fire-flues), a short earthenware or porcelain pipe is inserted, and the aspirating tube fixed in it by some cement, fire-clay, etc.

The porcelain or quartz tubes used for aspirating *hot* gases should be of such a length as to project a good deal on the outside. This projecting part may be filled with asbestos or glass-wool, in order to retain soot, ashes, etc., as shown in Fig. 1.

For taking gas samples from Bessemer converters, F. Fischer (*Z. Verein. deutsch. Ingen.*, 1902, pp. 1006 and 1367) employs the aspirating arrangement shown in Fig. 2. A porcelain tube *c* is placed inside an iron tube *b*, the two being held together at *a* by a collar of fireclay; the porcelain tube projects about 5 cm. beyond the iron tube. This apparatus is placed horizontally across the top of the converter, in such manner that the end of the porcelain tube is just over the gas current. A glass tube *z* is joined to the porcelain tube by a cement of clay and of sodium silicate solution, and at its other end is connected by india-rubber tubing *g*, with a number of glass bulbs, *n*, *n*, with capillary entrance- and exit-tubes. By means of an aspirator (which may be a water-vessel of the usual shape, or an india-rubber pump) the gases are aspirated out of the converter into the glass bulbs, and once every two minutes a bulb is removed after sealing off the capillary ends. In order to perform this operation in the open air, Fischer employs the small oil-lamp shown in Fig. 3, in half its real size. *d* is the wick-holder; B a tin-cap, with air-holes, *c*, *c*, at its lower end, a larger orifice at the top, and a circular side-hole *e*, from which issues the flame blown out by the point *n* of a blowpipe.

FIG. 2.

Frequently *metallic* aspirating tubes (made of iron, brass, copper, silver, platinum) are employed. They are, of course, not liable to breaking, but can only be employed where the temperature does not reach the softening or fusing point of the metal in question, and where no chemical action of the gas on the metal can take place. Owing to their great conductivity for heat, which might destroy the corks or india-rubber in contact with the metal, they must in many cases be provided with a cooling arrangement. For this purpose Winkler recommends an arrangement shown in Fig. 4.

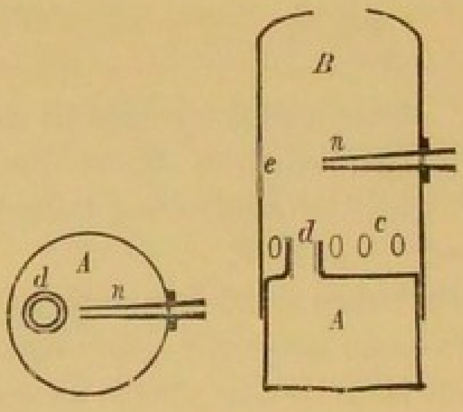

FIG. 3.

Three concentric copper tubes, of 1 or 2 mm. metal thickness, are connected in the way shown in the figure. The innermost tube *a* is 5 mm. wide; this is the aspirating tube. It is surrounded by tube *b*, 12 mm. wide, which is soldered up tight at one end, the other end towards A being left open. The side branch, *d*, with a stopcock, admits the cooling-water.

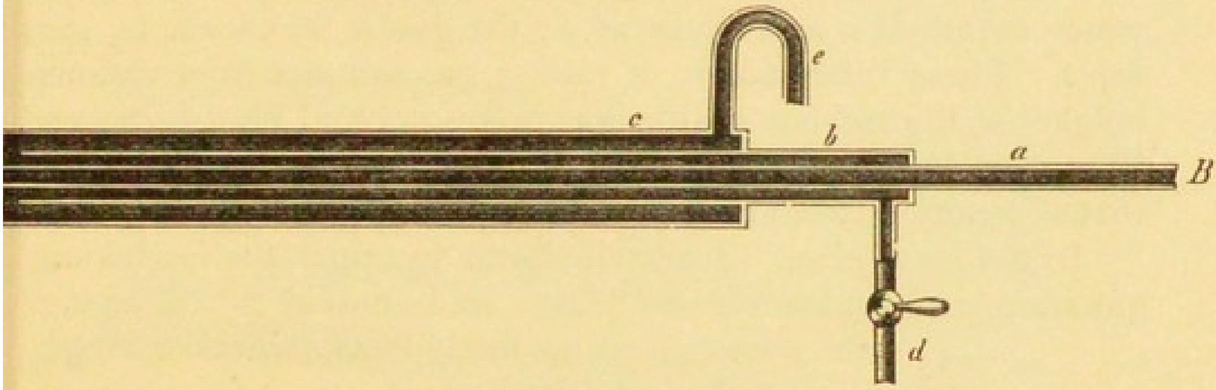

FIG. 4.

This tube is again surrounded by tube *c*, 20 mm. wide, which at the end A is soldered to tube *a*, and at the other end (near B) to tube *b*. Tube *c* is also provided with a branch *c*, through which the cooling-water, introduced by *d*, which has got heated on its way through tubes *b* and *c*, runs out. The length of tube AB may vary according to circumstances; usually about 2 feet will suffice.

This apparatus is placed in the furnace wall, in which a suitable hole has been made. The stopcock *d* is connected by an india-rubber pipe with a water pipe; it is then opened, and as soon as the water issues at *e*, the end A is introduced into the furnace, and the joint is made good by a wet mixture of fireclay and common clay. End *a* is now connected with an aspirator and with the reservoir for the gas to be sampled.

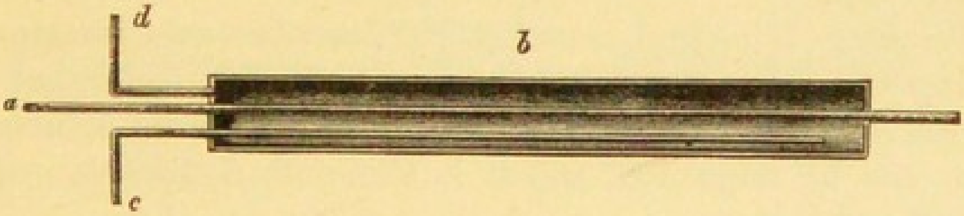

FIG. 5.

Drehschmidt (Post's *Chem. Techn. Anal.*, 3rd ed. p. 110) employs the simpler arrangement shown in Fig. 5. The aspirating tube *a*, 4 or 5 mm. wide, is surrounded by a jacket *b*, closed at both ends, into which cold water is introduced by pipe *a*, and runs out continuously at *d*. The pipes are made of copper and the joints are brazed.

Treadwell (*Quant. Anal.*, 5th ed. p. 600) recommends a similar arrangement, the St Claire Deville cold-hot tube, made of iron, as shown in Fig. 6. A rapid stream of cooling-water enters at *a* and issues at *b*; the gas is taken out by the tap *c*. These tubes admit of taking gas samples from various heights of the red-hot coal in gas-producers and blast-furnaces. Care must be taken to run the water through with such rapidity that it comes out cold at *b*.

In the same place Treadwell shows an apparatus for taking gas samples from inaccessible places, and another for collecting the gases given up freely from mineral springs, or absorbed in spring water.

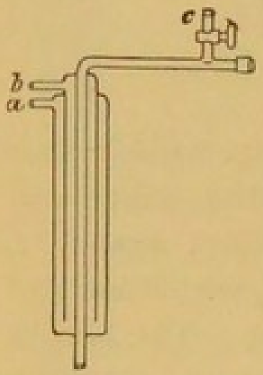

Fig. 6.

Fischer (*Dingl. J.*, ccxxxii. p. 528) points out that, where *iron* tubes are employed for aspirating the gases, the rust forming thereon may greatly alter the composition of the gases.

In very hot gases the constituents may be in a state of dissociation, and if during the aspiration they are rapidly cooled, carbon monoxide may be found co-existing with free oxygen, whereas in gradual cooling these two would combine to form CO_2.

Winkler (Winkler-Lunge,[1] p. 10) describes an apparatus for cooling the gases by immediate contact with water, but this process can be employed only where the gases soluble in water can be neglected, and it is therefore applicable only in exceptional cases.

Gray's automatic aspirating apparatus is described on p. 11.

ASPIRATING APPARATUS.

Wherever the gas to be sampled is under a higher than the atmospheric pressure, as a rule no special apparatus is needed for taking the samples. In the contrary case, where the gas

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[1] By this designation ("Winkler-Lunge") we quote Winkler's *Handbook of Technical Gas-Analysis*, translated by Lunge, second English edition, London, 1902.

does not of its own accord enter into the absorbing tubes or other analytical apparatus, special aspirators must be employed which may be "dry" or "wet" aspirators.

As dry aspirators, in many cases *india-rubber hand or foot blowers*, of the usual commercial description, may be used for taking the samples. Such blowers are shown in Fig. 7. The india-rubber vessel A is closed at both ends by wooden bungs or corks, containing inside a simple kind of leather clock-valve. Through one of these passes the aspirating tube *a*, through the other the discharging tube *b*. On compressing the vessel A by hand or foot, its gaseous contents are forced out through *b*; where the pressure is relaxed, A resumes its former shape, and thereby aspirates gas through *a*. By repeating this manipulation, considerable quantities of gas may be aspirated within a short time. No confining liquid comes into question in this case, but this contrivance can only be used where there is an ample supply of the gas to be examined, for the air previously present in the blower must be completely driven out and replaced by an excess of the gas to be analysed.

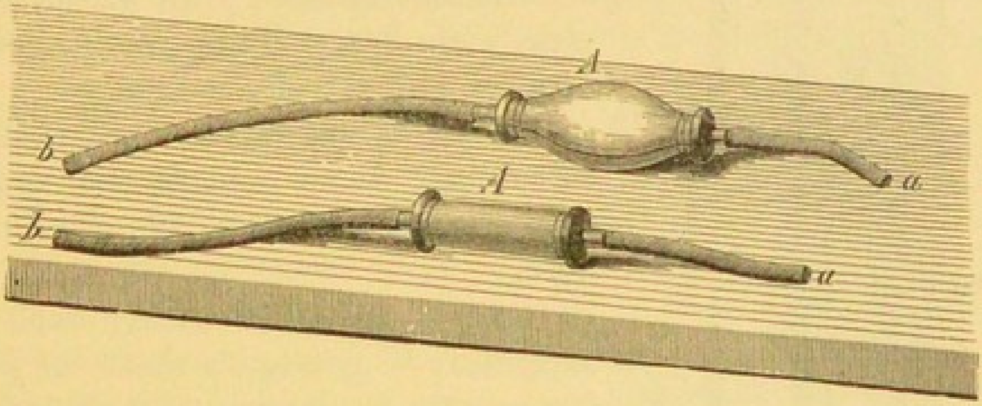

FIG. 7.

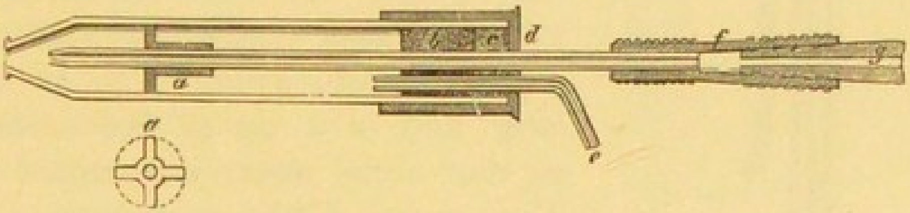

FIG. 8.

Fig. 8 shows a *steam-jet aspirator*. A strong glass tube, or in cases where the gas does not act upon metal, a metallic tube, 3 cm. wide and 20 to 25 cm. long, has a tapering end, with a 6-mm. orifice. A steam-pipe passes through it, the end of which, tapering down to 2-mm. bore, ends about 12 mm. behind the orifice of the outer tube. Near this point the steam-pipe is held in its place by a wooden or metallic ferrule, *a*; at the other end it is tightly fixed in the cork *b*, which also holds the tube *e* for the gas to be aspirated; *c* is a layer of cement; *d* a metallic ferrule; *f* an india-rubber pipe with hemp lining, making connection with the steam-pipe *g*.

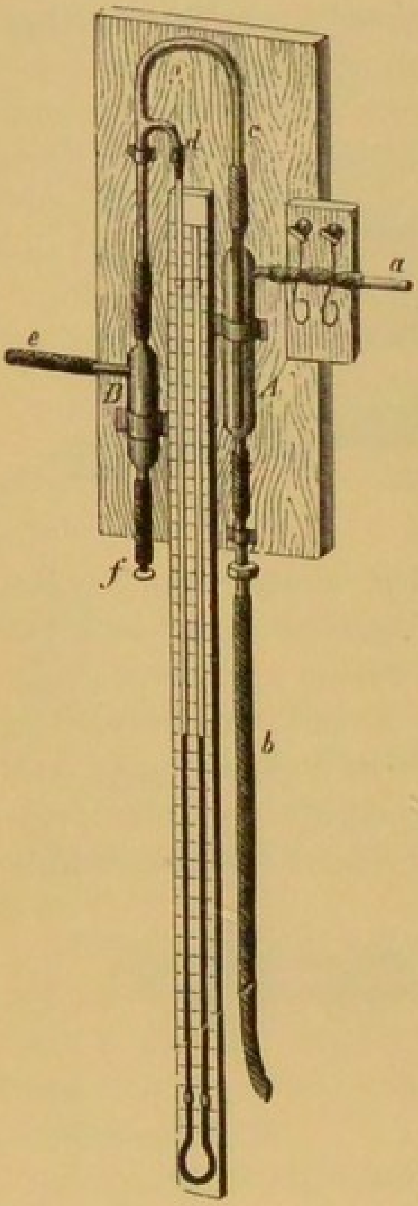

Fig. 9.

Of "wet" aspirators many descriptions have been constructed, only a few of which are to be mentioned here.

One of the most widely used wet aspirators is *Sprengel's water-air pump* (frequently but erroneously designated as "*Bunsen pump*") shown in Fig. 9. A cylindrical glass vessel A is at its contracted upper end connected by soldering with the glass tube *c*, the top of which is bent downwards and communicates with the glass vessel B. *c* descends inside A nearly down to its lower contraction, where it ends in a fine orifice. The bottom end of A is narrowed and connected with a lead pipe *b*, 8 mm. wide, 10 to 12 metres long, and bent up at the lower end so that some water is retained there. The vessel A also possesses a side-branch *a*, continued into an india-rubber pipe, connected with a water-reservoir or service-pipe. The flow of water can be once for all set to a certain rate by means of a screw clamp, and completely shut off by another clamp. When the running of water through *a* is started, pipe *b* is filled with a column of water balancing the weight of the atmosphere, and the water following this aspirates air (or gas) through *c*, which is yielded up at the lower end of *b*.

As long as c remains open, the air is continuously sucked in, while the flow of water is going on. If, however, c, or a space communicating with c, is closed, a vacuum is produced by the action of the water-barometer formed by the apparatus. Vessel B is not essential for the purpose of aspiration, but it serves for retaining any liquid carried on mechanically, which is from time to time discharged through f. Tube d is connected with a mercurial pressure gauge, which indicates the progress of the evacuation. Tube e is connected with the space to be evacuated, or from which a sample of gas is to be taken.

If the Sprengel pump is not to serve for completely evacuating the air from a given space, but only for aspirating gases, tube b need not be more than say, 1 metre long. In lieu of a lead tube, it may then be an india-rubber tube, closed at its lower end by a bent glass tube.

An improved form of mercurial gas-pumps is that constructed by Töpler which is sold by all dealers in chemical apparatus.

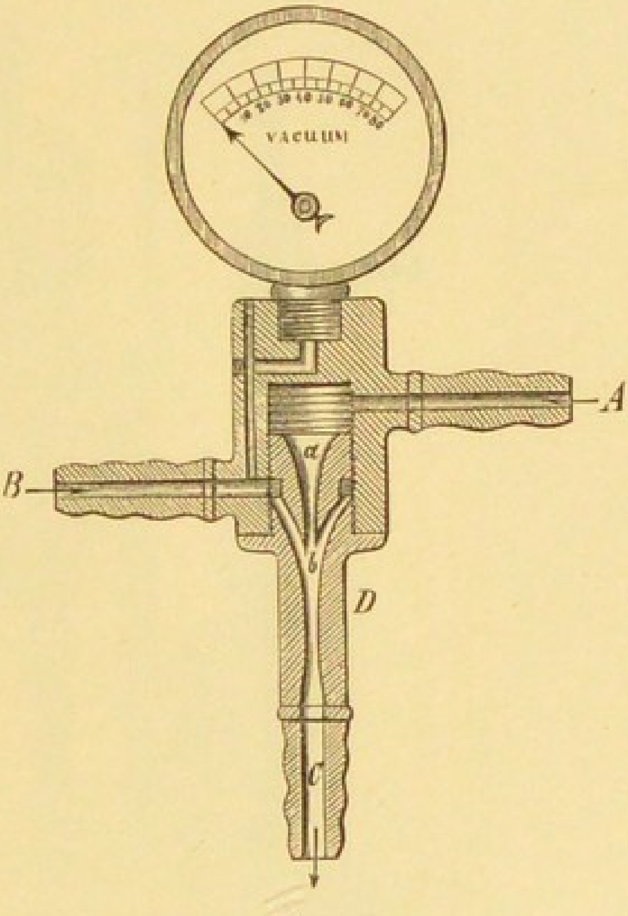

Fig. 10.

A number of *water-jet pumps* have been constructed by various inventors, *e.g.* Arzberger and Zulkowsky, H. Fischer, Körting Brothers, Ph. Schorer. They require no special height of fall for the waste water, but a head of 5 to 10 metres water for feeding. As an example of the way in which they work we refer to Fig. 10. The water enters at A, issues from the conical tube a, 1 mm. bore, carries along the air entering through B, passes the contracted part b, and runs off at C. The three tube-ends, A, B, and C, are connected by elastic tubing with the corresponding pipes.

Hardly less efficient are the various water-jet pumps made of glass, which can be connected with any water-tap by means of thick india-rubber tubing. We show here in Fig. 11 Finkener's aspirator, where the water enters from the service-pipe through the tube *a*, drawn out to a point; it runs away through tube *e*, which is widened at the top and bottom; the air aspirates through *b* and forms a frothy mixture with the water issuing at *c*. This tube is made in two pieces, connected by an india-rubber tube in order to diminish its fragility. Geissler's water-jet aspirator, shown in Fig. 12, can be understood without special explanation.

FIG. 11.

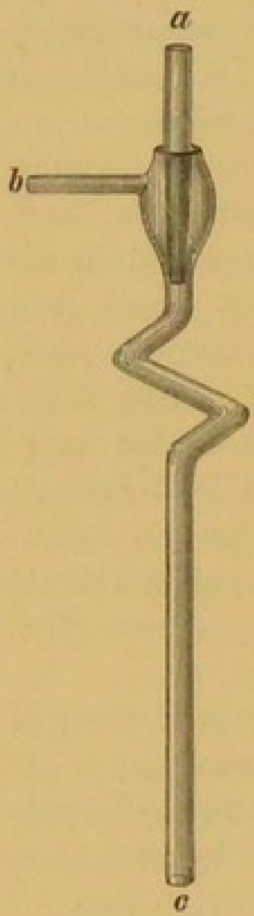

FIG. 12.

In many cases the gas-burette or the gas-collecting bottle themselves are employed as aspirators, by being filled with water, which is either run off within the space containing the gas to be examined, or after connecting the apparatus with the aspirating tube.

For collecting somewhat large quantities of gas, *aspirating* *bottles* may be employed as shown in Fig. 13. The bottle A is placed on a wooden stool; its india-rubber stopper is provided with a glass stopcock *a* and a tube *b*, reaching nearly down to the bottom of A, and connected by elastic tubing with a straight glass pipe acting as a syphon. The elastic tube can be closed entirely or partially by a screw clamp. Before taking the sample, bottle A is filled with water through tube *b* in such manner that no air-bubbles remain and that the water rises up to the stopcock *a*. Now all the air is removed from pipe *a* by means of the pump *c*; and the gas is aspirated by allowing the water to flow out into B. Such an arrangement can, for instance, serve for continously taking a sample from the main current of gases developed during a length of time.

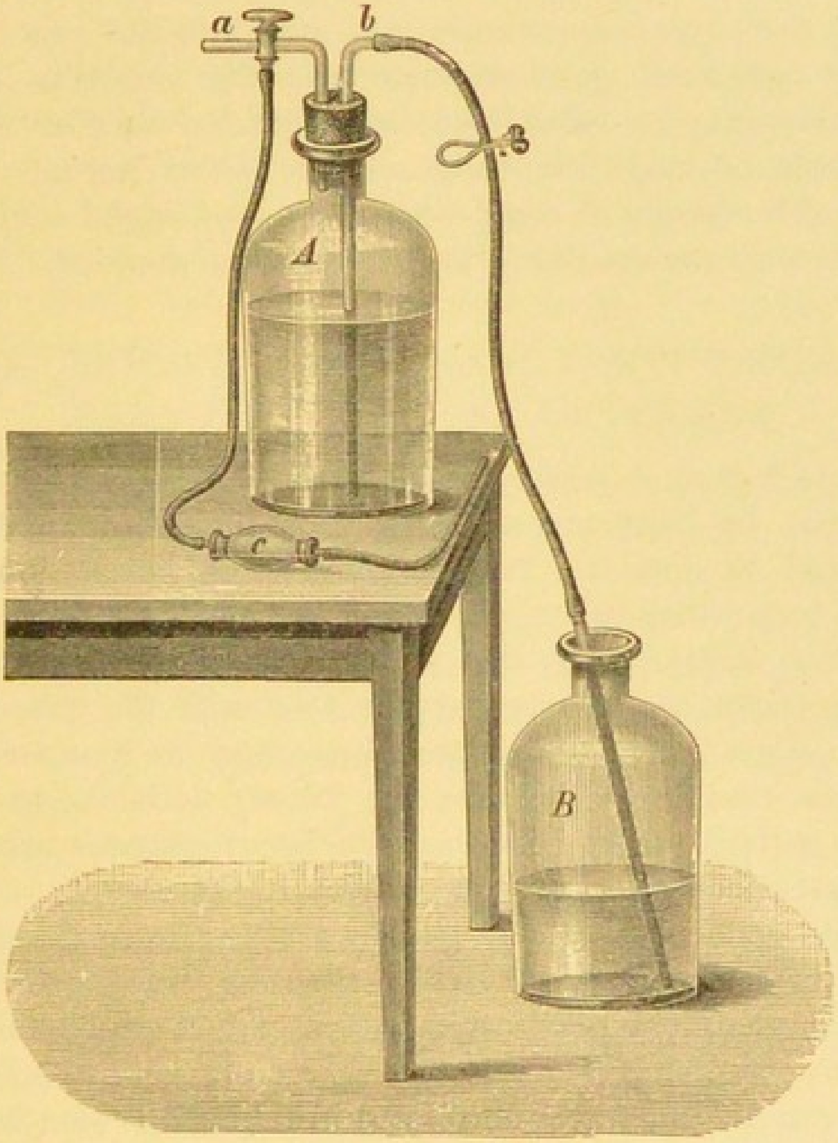

FIG. 13.

Aspirators of the same class, but made in a more substantial manner, are sold by most dealers in chemical instruments.[1]

An automatic gas-sampling apparatus, which permits of regularly taking samples from a current of gas, and thus to obtain an average sample, is described by Thomas Gray in *J. Soc. Chem. Ind.*, 1913, p. 1092. From a collecting vessel filled with mercury, water, or an aqueous solution of glycerin or magnesium chloride, the confining liquid is constantly running out, and thus gas is constantly aspirated into the vessel. The ordinary industrial gaseous fuels and the products of their combustion may be stored over concentrated aqueous solutions of glycerin or magnesium chloride for short periods without considerable change of composition, but prolonged contact and agitation with the confining liquid should be avoided.

VESSELS FOR COLLECTING, KEEPING, AND CARRYING SAMPLES OF GASES.

Unless it is unavoidable, samples of gases taken for analysis should not be kept for any length of time, but ought to be transferred at once to the gas-burette or absorption bottle, in order to be instantly analysed. Where it cannot be avoided to employ water-luting, the water must be brought merely into superficial and momentary contact with the gas, and *the gas should not pass through the water itself*, as it must do in a pneumatic trough. Otherwise the solvent action of the water, which is entirely different towards different gaseous substances, would essentially alter the composition to the gas.

If the collection of the gas in a separate vessel for the purpose of keeping it for some time or transporting it to some distance must needs take place, care must be taken not merely to completely exclude any access of air to it, but also to entirely remove the water employed in taking the sample, which would exercise a solvent action on some of the constituents of the gas. If the sampling is carried out without contact with water, by means of an india-rubber pump and a dry collecting vessel, or by aspirating it through the same, this operation must be continued long enough to ensure the *complete* expulsion of all air.

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[1] Some of these are described and illustrated in Winkler-Lunge, pp. 17 to 20.

India-rubber collecting vessels should, as a rule, be avoided (cf. *suprà*, Lunge and Harbeck, p. 4), even if their inside surface is protected by a coat of grease, because several gases, especially sulphur dioxide and hydrogen, are diffused through their walls. It has been found, however, that, for instance, mixtures of oxygen, nitrogen, carbon dioxide, and carbon monoxide (that is, the gases produced by the combustion of fuel) can be kept unchanged in such vessels for several hours, but not till the next day.

Glass collecting vessels (*e.g.* that shown in Fig. 2, p. 6) should be provided at both ends with tightly closing glass taps, or with capillary ends which are sealed by the lamp after introducing the gas. In order to transfer the gas afterwards to a gas-burette, a file stroke is cautiously made on each of the capillary ends; narrow india-rubber tubes are slipped over the capillaries, which are filled with water and closed by means of glass rods or pinchcocks. Now the ends are broken off within the india-rubber tubes by pressure from without, after connecting one of them with the gas-burette (previously filled with water). The other end is made to dip into a vessel also filled with water. The closing-rod is removed below the water, and the water contained in the burette is run off so that it is filled with the gas, the place of which in the collecting tube is taken by water. Treadwell (*Quant. Anal.*, p. 610) describes a similar method for transferring the gas from the glass tubes to a burette.

In many cases if the analysis can be carried out shortly after collecting the gas, it is not necessary to close the collecting glass tubes by sealing the capillary ends before the lamp; they may be closed by a short elastic tube provided with a pinchcock, or a bit of glass-rod with rounded ends, by well-ground-in glass taps.

Where for gas-analytical purposes *glass stopcocks* are employed, these must be kept tight by proper lubrication. Dennis (*Gas-Analysis*, p. 115) describes for this purpose the following preparation, which does not deteriorate on keeping, does not work out at the ends of the key, and gives off no hydrocarbon vapour. "Place in an evaporating dish twelve parts of vaseline and one part of paraffin-wax. Heat this mixture over a Bunsen flame, and maintain the contents of the dish at a temperature that will keep the materials fluid, but will not cause the mixture to emit fumes. Drop in successive portions of soft black rubber clippings, and stir the mixture after each addition until the rubber is completely dissolved. After about nine parts by weight of rubber has been added, take out a small sample of the lubricant on the end of a stirring-rod, allow it to cool, place it on the ball of the thumb, squeeze it with the end of the middle finger, and then rapidly tap the finger upon the thumb at the point covered by the lubricant. If on this treatment the lubricant forms light, feathery particles that float off in the air in fine flocks, the proper mixture has been reached. If the lubricant does not behave as described, stir in more rubber and test again. About ten parts by weight of the rubber will usually be required for the above amounts of vaseline and paraffin. In lubricating a glass stopcock, the key and barrel should first carefully be cleaned, and then the thinnest possible film of vaseline be rubbed over the surface of the key of the stopcock. The lubricant is then rubbed over the key, which is next inserted in the barrel and turned around until the lubricant is evenly distributed over the surface."

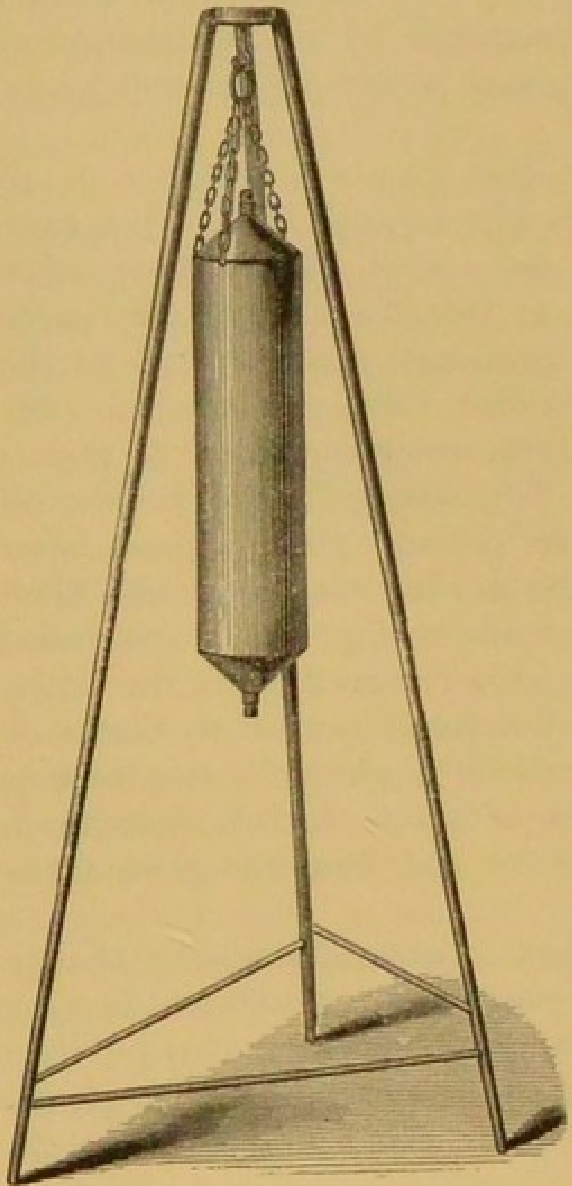

FIG. 14.

Wempe (*Z. angew. Chem.*, 1914, i. p. 216) describes a collecting-pipe for gases without a tap, and another with a glass valve.

For collecting and transporting larger volumes of gases which have no action on zinc, Winkler recommends vessels made of *zinc*, as shown in Fig. 14. They are cylinders, 50 cm. long and 16 cm. wide, with conical ends, 5 cm. long, and hold 10 litres of gas. They terminate at each end in necks of 15 mm. diameter, which are tightly closed by soft india-rubber plugs. The vessel is hung in a stand from three brass chains fitted at the top in a ring, and can thus be conveniently carried by hand even when filled with water. The gas sample is collected by putting the vessel in the proper place and running the water out. If it is desired to produce a slow or specially regulated outflow, the solid bungs are replaced by bungs fitted with glass tubes and provided with screw pinchcocks. Such vessels are employed in large numbers for taking samples of the pit gases in the Saxon coal-pits, and sending them for analysis to the Freiberg Mining Academy.

For collecting the gases from mineral springs, apparatus have been constructed by Ramsay and Travers (*Proc. Roy. Soc.*, 1896, p. 442), by Tiemann and Preusse (*Berl. Ber.*, 1879, p. 1768), by Henrich (*ibid.*, 1908, p. 4199), by Knud and Ruppin (Hempel's *Gasanal. Methoden*, 4th ed. 1913, p. 10).

THE MEASUREMENT OF GASES.

The volume of gases can be found either by directly measuring it, or, in some cases, by titration or gravimetric analysis. In this section we treat only of the direct measuring of the gas volume.

The tension, and therewith the volume of gases, depends upon—

1st. The pressure.
2nd. The temperature.
3rd. The state of moisture.

These conditions may be very different to begin with, and may vary during the analysis even from one observation to another. For very rapid technical estimations of the constituents of a gas these differences may be neglected; but even for many technical and for all accurate purposes, the gas volumes must be reduced to fixed conditions called the "normal" state, viz., to the barometric pressure of 760 mm. mercury, to a temperature of 0° C., and (for scientific purposes) to a state of absolute dryness. For technical purposes the last-named correction is frequently not made. The expansion by heat is $\frac{1}{273}$ of the volume of the gas at 0° for each degree centigrade.

All these corrections are embraced in the following formula, in which V signifies the corrected volume; V the volume observed at the barometric pressure B ruling at the time of the observation; t the temperature of the gas; and f the tension of aqueous vapour at the temperature t (as shown in the table at p. 25):—

$$V_0 = \frac{V \times 273 \times (B - f)}{(273 + t) \times 760}.$$

For example, we have found the gas, saturated with moisture, to occupy at 738 mm. pressure at 20° C., a volume of 1000 c.c. Its volume in the dry state at normal temperature and pressure will be:—

$$V_0 = \frac{1000 \times 273 \times (738 - 17{\cdot}4)}{(273 + 20) \times 760} = 884{\cdot}4 \text{ c.c.}$$

Wendriner (*Z. angew. Chem.*, 1914, i. p. 183) gives a formula for reducing gas volumes to the normal state by means of logarithms and special tables.

Tables for the reduction of the volume of gases to normal temperature and pressure, which replace the use of the above formula by a simple reading, are given in Lunge's *Technical Chemists' Handbook*, 1910, pp. 38 to 52.

This reduction to the "normal" state may be omitted in technical estimations which are rapidly performed, since material changes of pressure and temperature need not be expected in such cases. Variations of the barometric pressure by ± 1 mm. change the volume of a gas by ∓ 1 per cent.; variations of the temperature by ± 1° C. cause a change of ± 0·3 per cent.

It is therefore of great importance to *keep the temperature of a laboratory for gas-analysis as uniform as possible.* Wherever it is possible, a room with its window looking north is preferable.

When a gas is estimated by titration or by gravimetric analysis, its volume is at once calculated in the corrected state. If one of the gaseous constituents has been estimated, say, by titration, and another volumetrically, it may be desirable to calculate the volume which the former would occupy at the then existing state of barometric pressure and temperature, and in a state of saturation with marsh. The following formula serves for *reducing the volume of a gas from the normal state to that which it would occupy at a different pressure and temperature, and in a state of complete saturation with moisture*:—

$$V = \frac{V_0(273 + t)760}{273(B - f)},$$

where V, V_0, t, and f have the same meaning as *suprà*.

Apparatus for the mechanical reduction of the volumes of gases to the normal state without observing the barometer and thermometer.—An apparatus for this purpose was described by Barnes (*J. Chem. Soc.*, xxxix. p. 463), Vernon Harcourt in 1883, Kreusler (*Ber.*, 1884, p. 29). Winkler (*ibid.*, 1885, p. 2533) and Lunge (*Chem. Ind.*, 1885, p. 163) have described more convenient apparatus for the same purpose. Lunge's apparatus is shown in Fig. 15. An iron stand with two clamp-arms carries two perpendicular glass tubes, connected at the bottom by a thick india-rubber tube; one of these, A, is the measuring-tube, the other, B, the "level-tube." Tube A is enlarged at the top into a bulb and is closed by an absolutely tight tap. (Experience has shown that no ordinary glass taps hold tight in the long run; the means of attaining this end will be described later on in connection with the "gas-volumeter.") A holds exactly 100 c.c. from the top to the zero mark on the stem. The division marked on the cylindrical part extends from the zero point to 5 c.c. upwards and 25 c.c. below, so that volumes of from 95 to 125 c.c. can be read off accurately to 0·1 c.c. These two

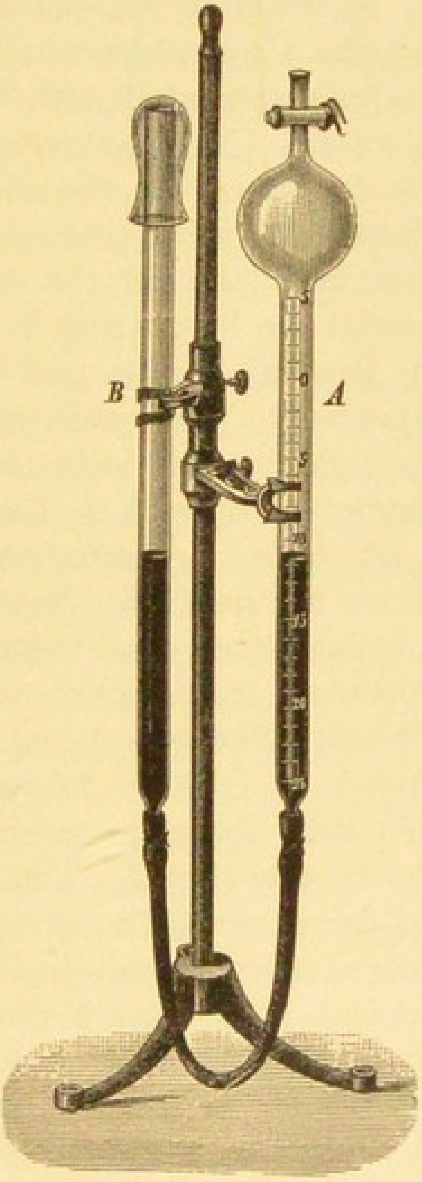

FIG. 15.

extreme values would correspond to 100 c.c. air under normal conditions, saturated with moisture, when brought to 800 mm. barometric pressure and 0° *t* on the one side, or to 700 mm. pressure and 30° *t* on the other side, which limits embrace all values occurring under ordinary circumstances. Tube A is held vertically in the lower clamp, the division being completely in view. The level-tube B is open at the top, which is protected by a dust-cover. B is held in the upper clamp of the stand, and can be moved upwards or downwards by means of a screw-clamp. It holds about 30 c.c.

In order to set the apparatus once for all for permanent use, the air contained in A is for ordinary purposes of technical analysis saturated with moisture, by introducing a few drops of water. (In those cases where the gas to be measured is in the dry state, *e.g.* the nitric oxide given off in the testing of nitrous and nitric compounds by means of the nitrometer, to be described later on, the reducing-instrument is adapted to this special use by putting in a drop of concentrated sulphuric acid, in lieu of water, and making the subsequent calculation accordingly.) A sufficient quantity of mercury is poured in through B, the instrument is placed into a room of even temperature, with a barometer and thermometer, and after a few hours, or better the next day, both of the latter instruments are read off. According to the formula given on p. 20, it is calculated what volume 100 c.c. of air, assumed to be in the "normal" state, would occupy under the actually existing conditions. The tap at the top of A being left open, tube B is raised or lowered to the point where the mercury level in this tube indicates precisely the calculated volume, and the tap is now closed. The volume of air thus confined increases or decreases with every change of external pressure and temperature, exactly in the same ratio as other gaseous volumes present in the same room and intended to be measured, so that the "normal" volume of the latter can be calculated by simple proportion, after having brought the mercury in A and B to the same level and reading off the volume shown in A.

Lunge (*Chem. Zeit.*, 1888, p. 821; *Z. angew. Chem.*, 1890, p. 227) has described a modification of this instrument which yields the reduced volume by a simple operation, and also the preparation of such *reduction-tubes* in a state fit for carriage to a distance; but these modifications, as well as the original instrument, have become obsolete by his invention of the "gas-volumeter," described below.

The correction for pressure and temperature may be avoided in cases where mercury is employed as confining liquid by the employment of a *Compensator*, that is a glass vessel connected with the measuring apparatus by a capillary, in which there is a minute column of liquid. Any alterations of temperature and pressure influence the gas volume equally both in the compensator and the gas-burette, so that no corrections are required if the pressure is made equal in both apparatus. Such an apparatus has been described by Petterson (*Z. anal. Chem.*, xxv. p. 467), and improved by Hempel and Drehschmidt; we shall mention it later on in connection with Drehschmidt's methods for gas-analysis. Another such "compensator" has been constructed by Borchers (Ger. P. 259044).

An apparatus for the *automatic elimination of the influence of temperature in gas-balances* has been constructed by Knöll (Ger. P. 247738; *J. Gasbeleucht.*, 1913, p. 407). On the beam of the balance or in the balance case two vessels are fixed, one which is closed and entirely filled with mercury; the other vessel is open, and but partially filled with mercury.

Lunge's Gas-volumeter (Lunge, *Berl. Ber.*, 1890, p. 440; 1892, p. 3157; *Z. angew. Chem.*, 1890, p. 130; 1891, p. 410; 1892, p. 677) for the first time realised the task of doing away with all calculations for reducing a gas volume to the "normal state," that is usually to 0° C. and 760 mm. pressure, either in the completely dry state or when saturated with moisture, by means of a mechanical operation carried out in a minimum of time and with a maximum of accuracy, without any recourse to calculations or tables. And this is done not merely for relative measurements, that is for comparing various gas volumes with the initial volume of a gas to be analysed, but for absolute measurements, such as are required for the gas-volumetric analysis of liquid or solid substances.

The fundamental idea of this process is the following:—If a certain quantity of air contained in a "reduction-tube" is by means of a "level-tube" placed under such pressure that it occupies the same volume as it would occupy at 0° C. and 760 mm. barometric pressure, and if precisely the same pressure is exercised on another unknown quantity of a gas, the latter must equally occupy the volume corresponding to 0° C. and a pressure of 760 mm. This purpose is attained if, first, the level-tube is placed at such a height that the air contained in the reduction-tube is reduced to the volume corresponding to the "normal" state; if, second, the same pressure, by the application of a T-pipe, is made to act upon the tube or other vessel containing the gas to be measured; and if, third, the level of the mercury in the last tube or vessel is exactly the same as in the "reduction-tube."

This contrivance may be applied to a gas-burette, or any other apparatus in which gases are to be measured, more particularly also to the "nitrometer" to be described later on (for which purpose it was first employed). We show it in Fig. 16 in connection with a gas-burette A; B is the "reduction-tube" and C the "level-tube."[1] They are all joined by very strong elastic tubes to a three-way pipe (T-pipe) D, and they can be made to slide upwards and downwards in strong clips. (All these parts are here shown in their simplest form; they have been considerably improved in shape later on.) The gas-burette A is generally made to hold 50 c.c., divided in 0·1 c.c., or else it holds about 150 c.c., the upper 90 or 100 c.c. being formed as a bulb, and the graduation beginning only at 90 or 100 c.c., and reaching down to the bottom. Or else this tube has a bulb in the middle, and is graduated from 0 to 30, and again from 100 to 150 c.c., so as to admit of measuring either small or large volumes of gas without unduly lengthening the tube. Tube B is made exactly like tube A in the gas-reduction apparatus (Fig. 15, p. 19), and is filled with exactly 100 c.c. of air, calculated for 760 mm. pressure and 0° C., precisely as stated in that place. This air must be either saturated with moisture by previously introducing a few drops of water, or else completely dried by means of a drop of concentrated sulphuric acid. In the first case the instrument is best adapted for the

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[1] The tubes E and F serve for the analysis of nitrous vitriol, to be described in a later chapter, and need not be noticed in this place.

measurement of moist gases, in the second for that of dry gases. It is set once for all by observing the state of the thermometer and barometer, calculating the volume which 100 c.c. of dry (or

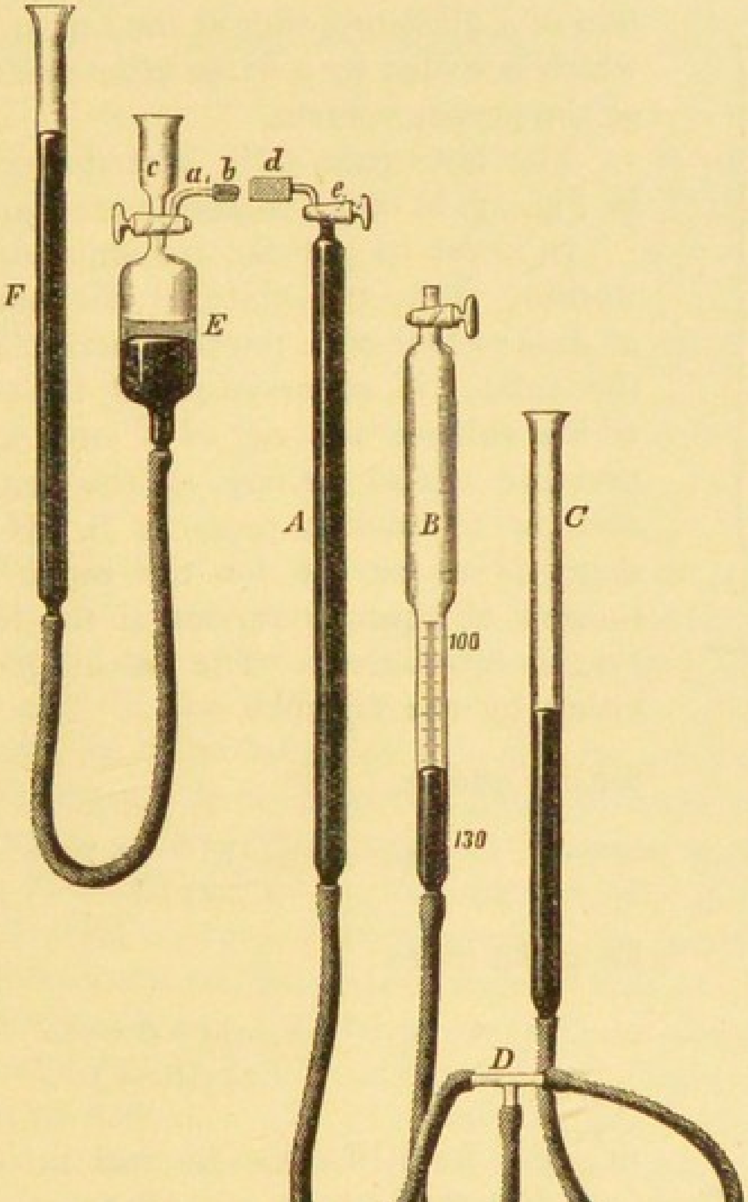


FIG. 16

moist) air would occupy under the conditions observed by means of the formula given in p. 18, setting the level of mercury at the corresponding place, and shutting the stopcock at the top. If this stopcock shuts air-tight, the reduction-tube holds for ever a volume of air, corresponding to 100 c.c. at 0° and 760 mm. pressure. Glass taps, securing a permanently tight closing fit have been constructed by Göckel (*Z. angew. Chem.*, 1910, pp. 961 and 1238; they are, for instance, manufactured by Alt. Eberhard and Jaeger, at Ilmenau). Or else tube B, in lieu of a glass tap, ends at the top in a capillary, which is sealed by a flame after setting the tube at the proper volume.

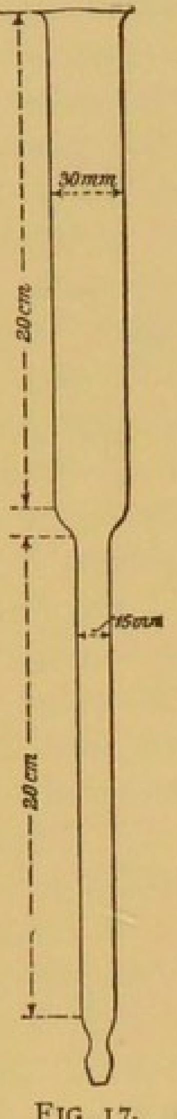


FIG. 17.

The level-tube C is best shaped as shown in Fig. 17, in order to save mercury.

In order to put the reduction-tube into its working state, the state of the barometer B, as well as that of a thermometer placed beside the tube t is observed; and it is calculated which volume 100 c.c. of 0° and at 760 mm. pressure would occupy at the temperature t and the barometric pressure B. If the instrument is to be set for the moist state, the tension of aqueous vapour at the temperature $t = f$ is introduced. The calculation is made either by the formulæ :—

for dry gases:

$$V_1 = \frac{V_0(273 + t) \times 760}{273B},$$

for moist gases:

$$V_1 = \frac{V_0(273 + t) \times 760}{273(B - f)},$$

or else from Tables 20 and 21 in Lunge's *Technical Chemists' Handbook*, 1910, pp. 38 to 52. Now, the top of the reduction-tube still being open, the level-tube is placed at the point indicated by V, which of course will be always above 100 c.c.; the stopcock is then closed (or the capillary end sealed up), and the instrument is now fit for use.

The following table shows the amount of f, viz., the tension of aqueous vapour in millimetres of mercury at the temperatures likely to occur in a chemist's laboratory, viz., between 10°

and 30° C. More detailed tables, extending from $-20°$ to 230° C., also for Fahrenheit degrees, are given in Lunge's *Technical Chemists' Handbook*, Nos. 23 to 25, pp. 54 to 58:—

TABLE I.—*Tension of Aqueous Vapour.*

Temperature. °C.	Pressure. mm. Hg.	Temperature. °C.	mm. °C.
+10	9·126	21	18·505
11	9·756	22	19·675
12	10·421	23	20·909
13	11·130	24	22·211
14	11·882	25	23·582
15	12·677	26	25·026
16	13·519	27	26·547
17	14·409	28	28·148
18	15·351	29	29·832
19	16·345	30	31·602
20	17·396		

According to whether it is more frequently required to measure gases in the dry state (*e.g.* in the nitrometric analysis of nitrous vitriol, of nitrates, of explosives, etc.) or in the moist state (*e.g.* in the usual technical analysis of fire-gases, producer-gases, etc.), the reduction-tube will be set for the dry or the moist state. It is, however, quite possible to employ that tube, when set for dry gases, to measure gases in the moist state, and *vice versâ.* If, for instance, dry gases are to be measured with a moist reduction-tube, the temperature is observed, the corresponding aqueous vapour tension f is taken from the table just given, and the mercury in the gas-measuring tube A is set at f mm. higher than in the reduction-tube, which had been set at 100 c.c. This is a very simple matter, as the gas-tube A is chosen of such width that each cubic centimetre occupies almost exactly a height of 10 mm., because in this case it is not necessary to apply a measuring-ruler. If, *vice versâ*, a dry reduction-tube is to be employed for moist gases, the mercury in the measuring-tube must be set by f mm. lower than in the reduction-tube, where it is always set at 100 c.c.—Or else, in order to measure a dry gas in A with a moist reduction-tube, it is first put into the moist state by introducing a drop of water, which is most easily done before allowing the gas to enter into A. For the inverse case, a moist gas is dried in A by a drop of concentrated sulphuric acid. In either case care must be taken not to allow the liquid to project above the mercury meniscus.

Reduction-tubes readily filled for Sales.—The construction of reduction-tubes containing the exact volume of 100 c.c. under standard conditions, and arranged in such manner that they can be kept in stock and sent out to customers by dealers in chemical apparatus, has been described by Lunge (*Z. angew. Chem.*, 1890, p. 228) and by Rey (*ibid.*, p. 229); but we merely refer to this, as difficulties have turned up in the practical application of such tubes.

As stated above, the connection of the tubes A, B, and C, in Fig. 16, p. 23, is effected by means of a ⊤-shaped pipe, to which they are joined by very thick *india-rubber tubing*. Such tubing, say of an external diameter of 13·5 mm. and a width of 4·5 mm., perfectly well stands the pressure of the mercury without blowing out, and even without the necessity of fixing it to the glass by means of wire, especially if the ends of the glass tubing are a little thickened. Elastic tubing of the just-mentioned size can be easily drawn over glass tubes of an outside diameter of 10 mm., or even a little more.

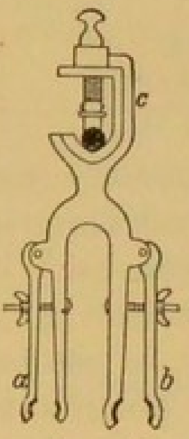


FIG. 18.

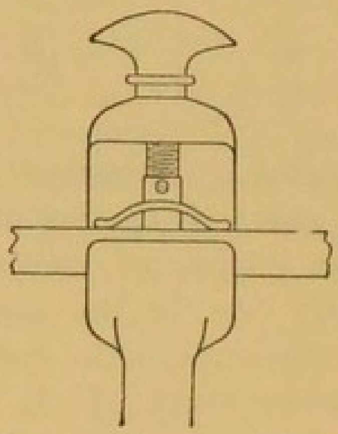


FIG. 19.

The tubes A, B, and C are held in strong *spring clamps* by friction, in such manner that they can be moved upwards or downwards, but do not descend by themselves. Such spring clamps sometimes fail to act properly after a time. This drawback is avoided by employing the double-screw clamps shown in Figs. 18 and 19, as supplied by C. Desaga in Heidelberg, and others.

A cast-iron fork carries in front two cork-lined clamps; a smaller one, *a*, for the reduction-tube (to be held below the 100 c.c. mark), and a larger one, *b*, for the level-tube. This fork is held on the stand by an ordinary clamp *c*, or one strengthened by a spring as shown in Fig. 19. By this fork-clamp the reduction-tube and the level-tube are combined to a set, movable in common upwards or downwards. When the gas-analytical operation has been finished, the set is put approximately at the level of the mercury in the gas-measuring tube; the level-tube is moved in its clamp *b*, in such manner that the mercury in the reduction-tube comes exactly up to the mark 100 c.c., and the fork-clamp, together with its two tubes, is moved through the clamp *c*, until the mercury in the reduction-tube and the gas-measuring tube is exactly on the same level. All this can be done in a few seconds, and much more easily than by means of separately moving spring clamps.

Since a difference of only 1° corresponds to a variation of 0·3 per cent., in the gas mixture, the gas-volumeter should stand in a room of uniform temperature and free from draughts.

Manipulation of the Gas-volumeter.—Suppose that a gas-analytic or gas-volumetric operation has been carried out in tube A (Fig. 16, p. 23). The reading of the gas volume is, in this case, not performed in the ordinary manner after putting the mercury in A and C on the same level. Only in such cases where a special side-bottle ("agitating vessel") has been used—*e.g.* for nitrogen estimations by the bromine-soda method, for the hydrogen peroxide methods, for carbon-dioxide estimations, etc.—it is necessary at first to place the levels in A and C at the same heights, in order to bring the gas in A to the atmospheric pressure ruling at the moment, whereupon the top of A is closed, without reading the gas-volume in that tube. If the gas has been evolved in A itself, or conveyed into that tube from another apparatus, the just-described operation does not, of course, come into question. The proper reading in A only takes place after placing the three tubes in such manner that the levels of the mercury in A and B are at the same height, and that in B is at the same time on the 100 c.c. mark. In that case the gases both in A and B are under such a pressure that the reading of the volume indicates the volume which they would occupy at 0° and 760 mm. This condition, of course, has been once for all established in B, and it now exists also in A, since the temperature and pressure (caused by the position of C) are the same as in B.

The setting of the tubes at the proper points is most easily and quickly done in the following way:—Tube A is fixed in the clamp, B and C are lifted up, but not equally; tube C must be placed so much higher that the mercury in B rises to the mark 100. Now B and C are simultaneously moved downwards in their clamps, in such manner that their mutual distance remains the same until the mercury level in B, that is the mark 100, is at the same level as the mercury in A. This simultaneous movement is not easily performed quite equally, but it can be at once completely corrected by a little shifting of the position of B. This double setting takes only a few seconds more time than the ordinary setting of the level-pipe for the gas-burette. Of course the placing of the mercury in A and B on the same level can be facilitated in the same way as in all similar cases, by sighting at the top of a wall or a window frame, or by a special straight-edge provided with a spirit-level as constructed by Lunge (*Ber.*, 1891, p. 3948).

The simultaneous moving of two tubes, fitted with mercury, is rather irksome if the spring clamps hold them tightly (as they ought to do). This drawback is completely avoided by employing the double screw clamp shown in Figs. 18 and 19, p. 26.

In those cases where *some other liquid*, apart from mercury, is introduced into the gas measuring-tube, its pressure must of course be taken into account as well. Thus, for instance, for the estimation of nitrogen by the method of Dumas, a special mark is made on the reduction-tube below the mark 100, corresponding to a tenth of the height of the potash solution contained in the gas measuring-tube. If the levels before reading are set in such manner that the mercury in the reduction-tube stands at 100, but in the gas measuring-tube on the same plane as the mark made below 100, the height of the column of potash liquor is thereby compensated.

It will be now clear that the employment of the gas-volumeter does away with the necessity of reading the thermometer and barometer, as well as that of making any calculations of the reduced volumes, whether by means of the afore-given formulæ or by special tables; the gas volumes are at once read in a state reduced to the "normal" conditions. Only as remarked on p. 24, according to the nature of the analytical operation, the reduction-tube must be arranged either for dry or for moist gases.

The principle of the gas-volumeter has been applied also to the exact estimation of carbon dioxide in carbonates, and to that of carbon in iron and steel (Lunge and Marchlewski, (*Z. angew. Chem.*, 1891, pp. 229 and 412); but we cannot discuss this here, and merely show the *decomposition flasks* constructed for that purpose, Figs. 20 and 21, which admit of heating the contents. The shape shown in Fig. 20 avoids the use of cork or india-rubber, but is more fragile than the shape Fig. 21.

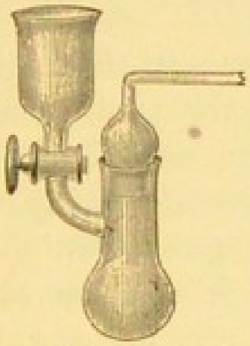


FIG. 20.


FIG. 21.

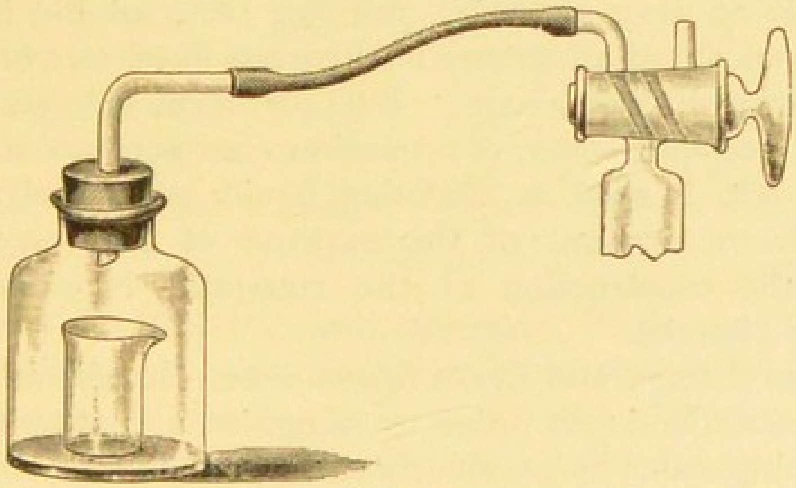


FIG. 22.

Fig. 22 shows the combination of the gas-volumeter (or of any other gas-measuring apparatus) with an *agitating bottle* for the estimation of carbon dioxide, for the estimation of nitrogen in ammonium salts or urea by means of brominated soda for the analysis of peroxide, permanganates, manganese ore, hypochlorites, etc., to be described in a later chapter.

Bodländer (*Z. angew. Chem.*, 1894, p. 425), under the name of "Baroscope," describes an instrument for calculating the *weight* of the gas in a burette from its pressure.

MEASURING APPARATUS FOR GASES.

It is hardly necessary to point out that all apparatus for measuring gases must be correctly graduated. Mostly the graduation indicates the volume in cubic centimetres, but its correctness must be checked by calibrating, either by the maker (who thereby undertakes a guarantee for it), or by the user. In gas-analysis proper it is usually sufficient if the volumes indicated on the burettes, etc., are equal amongst each other; but for the gas-volumetric testing of liquids or solids the volumes indicated must show the *real* cubic centimetres, since the volume of the gas given off in the operation is utilised for calculating a weight therefrom.

The first consideration is always with regard to the nature of the *confining liquid.* In most cases *mercury* is on principle the most suitable liquid for this purpose, since most gases do not act upon it (of course some gases, as chlorine and bromine vapour, do so very strongly), nor are they soluble in it, and since it does not at all adhere to the glass like water, or aqueous liquids, or even petroleum. But for technical gas-analysis, wherever possible, *water*, or sometimes an aqueous solution of common salt, is used as confining liquid, not merely or even principally on account of the expense of the mercury, but because the construction of the apparatus is often greatly facilitated thereby.

Pfeiffer (Lunge and Berl's *Chem. techn. Unt. Meth.*, 1911, iii. p. 252) recommends, in order to recognise a contamination of the confining water by previously employed alkaline absorbents, to add to it a little hydrochloric acid (20 c.c. normal HCl to 1 litre), methyl orange, also a little (0·5 g.) sodium salicylate, to prevent the development of fungi.

The same author, in order to promote the running off of the water from the glass sides of the apparatus and the formation of a clear meniscus, previously rinses the vessels with a mixture of strong sulphuric and nitric acid.

The nature of the confining liquid also influences the *meniscus-correction* which is not merely different for different iquids, but which must also be taken into consideration when weighing water or mercury into such vessels which in actual use are in an inverted position, the closed end then being at the top. Göckel justly points out that gas-measuring apparatus ought to be marked, *e.g.* "corrected for H_2O," or "corrected for Hg dry," or "Hg wet" (*Chem. Zeit.*, 1902, xxvi. p. 159). We hall treat of this below.

With respect of the use of water as confining liquid, the *olubility of gases in water* must be kept in view. The following able shows the absorption coefficients of various gases, that is he volume of gas absorbed by water of different temperatures, educed to 0° C. and 760 mm. pressure, if the gas itself is nder a pressure of 760 mm. These values are taken from Bunsen (*Gasom. Methoden*, 2nd ed. p. 384); Winkler (*Ber.*, xxiv. pp. 99, 3606, 3609); Landolt-Börnstein-Meyerhoffer, 3rd ed. p. 599; Bohr and Bock (*Wiedem. Ann.*, xliv. p. 318); Than (*Ann.*, cxxiii. p. 187). A more detailed table of the solubility of gases in water, extending from 0° to 100°, is given in Lunge's *Technical Chemists' Handbook* (1910), pp. 20 to 23.

TABLE II.—*Solubility of Gases in Water.*

	10°.	15°.	20°.	25°.	30°.	35°.
Oxygen	0·038	0·034	0·031	0·028	0·026	0·024
Hydrogen	0·020	0·019	0·018	0·018	0·017	0·017
Nitrogen	0·020	0·018	0·016	0·015	0·014	0·013
Chlorine	3·095	2·635	2·260	1·985	1·769	1·575
Carbon monoxide	0·028	0·025	0·023	0·021	0·020	0·019
Carbon dioxide	1·194	1·019	0·878	0·759	0·665	0·592
Hydrogen sulphide	3·520	3·056	2·672	...	...	...
Ammonia	910·4	802·4	710·6	634·6	...	...
Sulphur dioxide	56·65	47·28	39·37	32·79	27·16	22·49
Methane	0·042	0·037	0·033	0·030	0·028	0·025
Ethylene	0·162	0·139	0·122	0·108	0·098	...
Propylene	0·280	0·237	0·221	...	...	...
Acetylene	1·31	1·15	1·03	0·93	0·84	...
Atmospheric air	0·023	0·020	0·019	0·017	0·016	0·015

We see from this that water dissolves so much ammonia, sulphur dioxide, and chlorine that it cannot be employed as confining liquid in the presence of these gases. Its dissolving power for carbon dioxide, acetylene, propylene, and ethylene is also considerable; if these are present, the confining water should be previously shaken up with another quantity of the gas to be examined. Especially in the analysis of gaseous mixtures containing a high percentage of these gases their solubility in water, as well as that of atmospheric air, must be taken into consideration (*cf.* Stock and Nielsen, *Ber.*, 1906, p. 3889).

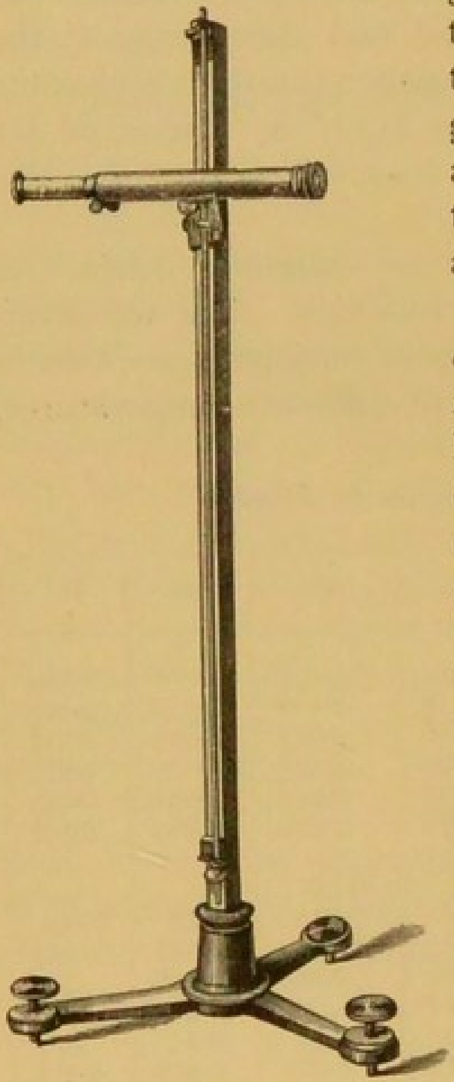
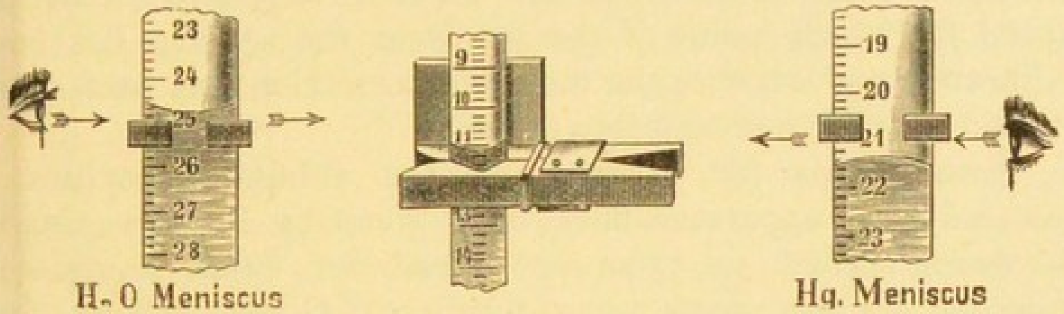


FIG. 23.

Contrivances for a Correct Reading of the Level of the Liquid.—The readings in the case of aqueous confining liquids are taken at the lowest point of the meniscus, where the coincidence with one of the marks of the graduation can be clearly recognised. Perfectly exact readings are taken by means of a magnifying glass, or with even more certainty through the telescope of a *cathetometer*, Fig. 23, such as serve for accurate observations of the barometer and thermometer. The telescope slides up and down on a triangular brass column, and can be easily adjusted in any place by a rack and pinion. The observations are best made from a distance of 2 or 3 metres.

This instrument is hardly ever used in technical gas-analysis, but for this as well the mistakes must be avoided which are caused by not holding the eye exactly on the level of the meniscus. Such mistakes cannot occur where the meniscus exactly coincides with a circular mark of the division, running right round the tube, but this, of course, is not the ordinary case. The "floats," which are employed in the ordinary burettes for volumetric analysis of liquids and solids, cannot be used in as-volumetric apparatus, and there are certain drawbacks onnected with them even in their proper sphere (Kreitling, *. angew. Chem.*, 1900, pp. 829 and 990; 1902, p. 4).

An excellent contrivance for avoiding the mistakes in eading burettes is that described by Dr H. Göckel in *Chem. eit.*, xxvii. p. 1036, by the name of *Visierblende* (say, *ighting-clamp*), and shown in Fig. 24 in its application both r water and mercury. The sighting-clamp is placed on the urette 2 or 3 mm. below the lowest point of the water eniscus, or above the top of the mercury meniscus, and



H_2O Meniscus

Hg. Meniscus

FIG. 24.

wing to the shape adopted by Göckel one and the same clamp an be applied to tubes of from 9 to 20 mm. diameter. This lack clamp produces a very sharp, black limiting-line. The arallax fault in reading is avoided by the fact that the opening f the clamp is exactly at a right angle to its horizontal level, nd small metal discs screwed on secure the fact that on pening and shutting the clamp its movement always takes lace in the same plane. Hence, in order to avoid the parallax ault, the eye need only be placed at such a height that he front and back edge line of the clamp coincide. Göckel's ighting-clamp is doing excellent service in many laboratories.

Very good service in reading the levels is also done by mploying a *straight-edge*, provided with a spirit-level, as escribed by Lunge in *Berl. Ber.*, 1891, p. 3948.

ADJUSTMENT OR CALIBRATION OF GAS-MEASURING APPARATUS.

Here we must distinguish between apparatus for gas-nalysis proper, where only relative measurements are required, nd apparatus for gas-volumetric analysis, where the absolute quantity of the gas must be ascertained (*v. suprà*, p. 30). We must also consider whether the gas is to be confined by water, or by mercury (in the case of nitrometers the confining liquid is sulphuric acid), and we must also take the meniscus correction for the confining liquids into account, in case the readings are made in places of unequal diameters of the tubes.

The capacity of gas-burettes, etc., intended to hold exactly 100 c.c. or any other definite volume between two glass stopcocks, such as Winkler's burette, is hardly ever correct, and the actual capacity should always be determined and the corrected value marked on the burette; it should further be noted for which point of the meniscus the reading has been calibrated, and whether the meniscus correction has been made for water or for mercury (see below).

Prescriptions for ascertaining the volume capacities of gas-analytical apparatus have been given by Bunsen (*Gasom. Methoden*, 2nd ed. pp. 55 *et. seq.*); Berthelot (*Traité pratique de l'analyse des gaz.*, 1906, pp. 215 to 217); Göckel (*Chem. Zeit.*, 1902, p. 195; *Z. f. Chem. App. Kunde*, 1907, p. 305); Schloesser and Grimm (*eodem loco*, 1907, p. 201). The last-mentioned paper, which is based on the researches made by the German Normal-Eichungskommission, will be especially taken into consideration.

We first quote the table (p. 35) they give for the *meniscus corrections* for water and mercury, which give these values both in cubic centimetres and in milligrams, viz., as the height of a cylinder of the diameter of the tube in question.

Calibration.—According to Schloesser and Grimm the calibration of gas-analytical apparatus is carried out in the following manner (principally founded on the prescriptions of the Imperial Normal-Eichungskommission):—

1. In the case working with *liquids adhering to the glass*, mostly *water*, and of apparatus which during the calibration are in the same position as in actual use, the calibration is carried out in the same way as for volumetric apparatus generally. The water is weighed in small stoppered *weighing-bottles* on an ordinary analytical balance. Its temperature must be taken with a correct thermometer to within ± 0·1° (this is sufficient for all cases, although the German Normal-Eichungskommission goes to ± 0·01°). The normal tempera-

TABLE III.—*Meniscus Corrections for Mercury and Water.*

Mercury.			Water.		
Diameter of tube. mm.	Correction.		Correction.		Diameter of tube. mm.
	In c.c.	In mm.	In c.c.	In mm.	
1	0·001	0·76	...	...	...
2	2	54	...	...	...
3	3	40	0·006	0·85	3
4	4	32	10	80	4
5	0·006	0·33	0·015	0·76	5
6	12	41	22	77	6
7	20	53	30	78	7
8	29	58	41	81	8
9	38	60	53	83	9
10	0·048	0·61	0·067	0·85	10
11	57	60	83	87	11
12	66	59	102	90	12
13	76	57	123	93	13
14	86	56	145	94	14
15	0·096	0·54	0·168	0·95	15
16	106	53	193	96	16
17	116	51	220	97	17
18	127	50	249	98	18
19	137	49	280	99	19
20	0·148	0·47	0·312	0·99	20
21	159	46	345	1·00	21
22	170	45	379	1·00	22
23	182	44	411	0·99	23
24	193	43	441	97	24
25	0·205	0·42	0·469	0·96	25
26	216	41	495	93	26
27	228	40	521	91	27
28	270	39	545	89	28
29	253	38	568	86	29
30	0·265	0·37	0·590	0·83	30

ture is 15°. If the temperature of the water exceeds 15°, use may be made of the following table, calculated by Schloesser for the expansion coefficient of glass = 0·000027, and the values for the expansion of water given by the Physico-technical Reichsaustalt. The figures of this table denote the number of cubic centimetres which must be subtracted from 1000 c.c. to give the volume of water which at *t*° fills a litre flask, calibrated at 15°, so that it occupies a volume of 1000 c.c. at 15°:—

TABLE IV.—*Volumes of Water at Temperatures from* 15° *to* 30°.

Temperature.	c.c.	Temperature.	c.c.
15° C.	0·000	23° C	1·348
16	0·130	24	1·563
17	0·272	25	1·788
18	0·42	26	2·023
19	0·58	27	2·267
20	0·76	28	2·520
21	0·94	29	2·782
22	1·14	30	3·053

The temperature of calibration should be stated as in the case of liquids, $\frac{15^\circ}{4^\circ}$, $\frac{20^\circ}{4^\circ}$, etc., since, if the calibration has been effected at 15°, determinations made at this temperature and, say, at 25°, are not equivalent.

The apparatus is placed in a perpendicular position; it is then filled up to the top with water, and this is run off into the weighing-bottles in quantities of from 2 to 10 c.c. according to the accuracy desired, in such manner that the outlet pipe constantly touches the wall of the weighing-bottle. The water is run off quickly to a few millimetres above the mark; one must then wait until the level of the water has become constant and then run it off exactly to the mark. The running-off must be performed by means of glass jets attached to the burette by means of a *very short* and elastic india-rubber tube. The outlet-opening of the jet must be as narrow as possible, because this causes the running-out to be slower and the after-running to be more quickly finished than in case of a wider outlet.

The operation is repeated at least once, in case of somewhat onsiderable deviations more frequently, and from the mean bservations a correction-table is calculated, which states the eal value of the readings, reduced to the " normal " conditions.

The time interval of two minutes before taking a reading, s recommended in the case of burettes, is not applicable to as-measuring tubes, since it depends on their form and iameter. In most cases the values given below for the time aken by the water used in gas-burettes to attain the final osition may be taken as correct :—

or 25 c.c.	3 minutes	For 125 c.c.	7 minutes
,, 50 ,,	4 ,,	,, 150 ,,	8 ,,
,, 75 ,,	5 ,,	,, 175 ,,	9 ,,
,, 100 ,,	6 ,,	,, 200 ,,	10 ,,

Before calibration the measuring apparatus must be horoughly cleansed. Any dirt present causes an irregular rmation of the meniscus; any traces of grease cause drops f liquid to be retained which influences the contents by volume. The cleansing must be performed mechanically by means of rushes, and chemically by means of a hot soap solution, or mixture of potassium bichromate and concentrated sulphuric cid; or in the case of obstinately adhering traces of grease, by cautious treatment with fuming nitric acid, until on rinsing ith water, free from any grease, this runs off completely verywhere. (Some operators use fluohydric acid or else trong caustic soda solution for cleansing, but neither of these hould be employed.)

When many calibrations have to be made, the weighings, hich take a good deal of time, may be replaced by reliable ormal measuring apparatus, which certainly do not afford he same certainty as weighings. The apparatus most usually mployed for this purpose is *Ostwald's pipettes*, Fig. 25. These ipettes are made to hold either 2 or 5 c.c., according to the egree of accuracy desired. They are attached to the bottom the burette, as shown in the figure; water of exactly easured temperature is poured into the burette, and by pening the pinchcock *a* also enters into the pipette, exactly p to the mark *b*. Now a weighing-glass is placed underneath, nchcock *d* is opened, and the water run out exactly down to ark *c*, waiting in the end one, or better two minutes, so as to et the last out-flowing parts into the weighing-glass. From three well-agreeing weighings of the contents of the pipette between marks *b* and *c*, an average is taken which holds good in all future, and from which the contents of the pipette are calculated for the "true litre."

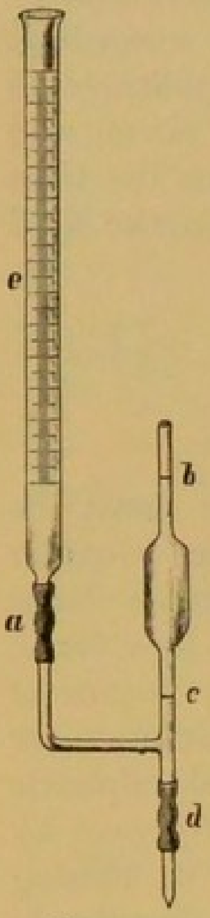


FIG. 25.

Cushman (*Chem. News*, 1902, lxxxv. p. 77) mentions an improvement on the Ostwald pipette which Ostwald himself had previously adopted. It consists in graduating the upper narrow tube, care being taken that the capacity of the pipette from the mark *c* to about the middle of the upper tube *b* is 2 c.c. It is then not necessary to determine the capacity of the pipette by a number of accurate weighings as above, but only to find the value of the pipette scale with regard to the burette scale by a few determinations. In calibrating, 2 c.c. at a time are allowed to pass from the burette into the pipette, and the height of the liquid in the latter noted; the corrections of the burette can thus be calculated. This calibration is of course only relative; if the absolute values of the graduations are required, the capacity of the pipette must be determined in the ordinary way. Or it may be ascertained by a few weighings up to which of the graduations on the upper tube the pipette has to be filled so that it holds exactly 2 c.c.; it is subsequently always filled up to this mark, and used for correcting according to the method described above, whereby the corrections to be applied to the readings of the burette can be found without much calculation. For calibrations according to the true litre, attention must be paid to the details now given.

The True Litre.—The "true litre" is the volume which 1 kg. of water at 4° occupies under standard pressure. If this space, or divisions corresponding to it, are to be marked off on a flask, or burette, etc., the position of the mark will depend on the temperature of the vessel. The standard temperature for this purpose at the National Physical Laboratory is 15° C.; that means that at a temperature of 15° the volume of the contents of a litre flask is the same as that of a kilogram of water at a temperature of 4°. The tables given on pp. 40-41 allow the adjustment to be made directly at any desired temperature and pressure, the weights which must be placed on the scale pan to effect this being given in each case. They have been calculated by the German Normal Standards Commission, and communicated by Schloesser (*loc. cit.*).

Any two correct measuring apparatus for a litre, or any subdivisions of this, if made of glass, and adjusted at different *temperatures*, differ only by the difference in the expansion of glass between the two temperatures, if water of the same temperature has been used in testing them. Therefore it is only necessary to calculate the weight which is in equilibrium with the weight of water occupying a true litre measuring apparatus for the normal temperature = 15°. If the temperature of the air does not greatly deviate from this, and the height of the barometer is not very far from 760 mm., sufficiently correct assumptions may be made for the factors which influence the buoyancy of the air, temperature, pressure, and the degree of moisture; and the reductions thus obtained may be combined with those due to the temperature of the water. The values in Table V. *A*, p. 40, can then be employed directly in order to find how the volume of a true litre should be marked off on a flask. If, *e.g.*, the air and the water have a temperature of 17°, the empty flask along with a kilogram weight is placed on one scale pan and brought to equilibrium by a tare on the other pan; the kilogram weight is then removed, and on the same side (that is, along with the flask) weights to the amount of 2·208 g. are placed; equilibrium is then re-established by filling the flask with water of 17°, and the volume occupied by this weight of water marked on the neck of the flask.

In the case of greater deviations of the temperature of the air from 15°, and of the atmospheric pressure from 760 mm., Table *B*, p. 41, is used to correct the values of Table *A*. If, *e.g.*, the height of the barometer is 720 mm., the temperature of the air 25°, that of the water 24·3°, the weight to be added for a litre is :—

From Table *A* . . .	3564 mg.
" *B* . . .	−92 "
	3472 mg.

The weight of the volume of water required to correspond to a true litre for the flask at 15° is therefore 1000 − 3·472 = 966·528 g.

For any other normal temperature (*t*) the amount:

TABLE V.—*Tables to be used in Calibrating for Reducing the Volumes of Gases to the "True Litre" Standard.*

A. Weight in milligrams to be added for 1000 c.c. The cubic coefficient of expansion of glass = 0·000027 at 0° C. Normal temperature = 15°. Height of barometer = 760 mm. Temperature of the air = 15°. Mean pressure of aqueous vapour = 8 mg. per litre.

t.	·0.	·1.	·2.	·3.	·4.	·5.	·6.	·7.	·8.	·9.	*t.*
5	1341	1340	1339	1338	1338	1338	1338	1338	1338	1338	5
6	1338	1339	1340	1341	1342	1343	1344	1345	1346	1348	6
7	1350	1352	1354	1356	1358	1360	1363	1366	1369	1372	7
8	1376	1380	1384	1388	1392	1396	1400	1404	1408	1412	8
9	1417	1421	1426	1431	1436	1442	1447	1452	1458	1464	9
10	1471	1477	1483	1489	1496	1503	1510	1517	1524	1531	10
11	1539	1547	1555	1563	1571	1579	1587	1595	1603	1611	11
12	1619	1628	1637	1646	1655	1664	1673	1683	1693	1703	12
13	1713	1723	1733	1743	1753	1764	1775	1786	1797	1808	13
14	1819	1830	1841	1853	1865	1877	1889	1901	1913	1925	14
15	1937	1949	1962	1975	1988	2001	2014	2027	2040	2053	15
16	2066	2080	2094	2108	2122	2136	2150	2164	2178	2193	16
17	2208	2223	2238	2253	2268	2283	2298	2313	2328	2344	17
18	2360	2376	2392	2408	2424	2440	2457	2474	2491	2508	18
19	2525	2542	2559	2576	2593	2610	2627	2645	2663	2681	19
20	2699	2717	2735	2753	2771	2789	2807	2826	2845	2864	20
21	2883	2902	2921	2940	2959	2978	2998	3018	3038	3058	21
22	3078	3098	3118	3138	3158	3178	3199	3220	3241	3262	22
23	3283	3304	3325	3346	3367	3388	3410	3432	3454	3476	23
24	3498	3520	3542	3564	3586	3609	3632	3655	3678	3701	24
25	3724	3747	3770	3793	3816	3839	3862	3886	3910	3934	25
26	3958	3982	4006	4030	4054	4078	4102	4127	4152	4177	26
27	4202	4227	4252	4277	4302	4327	4352	4377	4403	4429	27
28	4455	4481	4507	4533	4559	4585	4611	4637	4663	4689	28
29	4716	4743	4770	4797	4824	4851	4878	4905	4932	4959	29
30	4987	5014	5041	5069	5097	5125	5153	5181	5210	5239	30

temperatures of the air from 5° to 31° C.

mm.	650.	660.	670.	680.	690.	700.	710.	720.	730.	740.	750.	760.	770.	780.	790.	mm.
t 5°	−121	−106	− 91	− 77	− 62	− 47	− 32	− 18	− 3	+11	+26	+41	+55	+70	+84	5° t
6	124	109	95	80	66	51	36	22	7	+ 7	+22	37	51	66	80	6
7	128	113	99	84	70	55	40	26	11	+ 3	+18	32	47	61	76	7
8	131	116	102	87	73	58	44	29	15	0	+14	28	43	57	72	8
9	135	120	106	91	77	62	48	33	19	− 4	+10	24	38	53	67	9
10	138	124	109	95	80	66	52	37	23	8	+ 6	20	34	49	63	10
11	−141	−127	−112	− 98	− 84	− 70	− 56	− 41	−27	−12	+ 2	+16	+30	+45	+59	11
12	145	131	116	102	88	74	60	45	31	16	− 2	+12	26	41	55	12
13	148	134	119	105	91	77	63	49	34	20	− 6	+ 8	22	36	50	13
14	152	138	123	108	94	81	67	53	38	24	−10	+ 4	18	32	46	14
15	155	141	127	112	98	85	71	57	42	28	−14	0	14	28	42	15
16	−158	−144	−130	−116	−102	− 88	− 74	− 60	−46	−32	−18	− 4	+10	+24	+38	16
17	161	147	133	120	106	92	78	64	50	36	22	− 8	+ 6	+20	34	17
18	165	151	137	123	109	95	81	67	53	39	25	−11	+ 3	+16	30	18
19	168	154	140	127	113	99	85	71	57	43	29	−15	− 1	+12	26	19
20	171	157	143	130	116	102	88	74	61	47	33	−19	− 5	+ 8	22	20
21	−174	−161	−147	−133	−119	−105	− 91	− 78	−64	−51	−37	−23	− 9	+ 4	+18	21
22	177	164	150	137	123	109	95	81	68	54	40	26	−13	+ 1	+14	22
23	181	167	154	140	126	112	98	85	71	58	44	30	16	− 3	+11	23
24	184	171	157	144	130	116	102	88	75	61	47	33	20	− 6	+ 7	24
25	187	174	160	147	133	119	105	92	78	65	51	37	24	−10	+ 3	25
26	−190	−177	−163	−150	−136	−122	−109	− 95	−82	−68	−55	−41	−28	−14	− 1	26
27	193	180	166	153	139	125	112	98	85	71	58	45	31	18	4	27
28	197	184	170	157	143	129	116	102	89	75	62	48	35	21	8	28
29	200	187	173	160	146	132	119	105	92	78	65	52	38	25	11	29
30	203	190	176	163	149	135	122	109	95	82	69	56	42	29	15	30
31	206	193	179	166	152	138	125	112	99	86	73	60	46	33	19	31

$(t-15)0{\cdot}000027$ must be added to the above; thus for a normal temperature of 20° all the values of Table *A* must be increased by $1000\,(20-15)0{\cdot}000027=135$ mg. For a water temperature of 20°, $2699+135 = 2834$ mg. must therefore be added.

If a value differing from that given in these tables be chosen for the mean expansion coefficient of glass, then $1000\,(a'-0{\cdot}00027)(t-15°)$ must be added to the values of Table *A*, a' denoting the new coefficient of expansion of glass, and t the temperature of the water. The amount of this correction is always very small, and is hardly likely to be employed by the chemist in calibrating.

It is very useful to construct for each burette a table, showing the *true* contents for the cubic centimetres *read off.* Very conveniently these values are entered in a system of co-ordinates, in which the cubic centimetres read off appear as absciss values, the true cubic centimetres as ordinate values. By connecting the respective points, a curve is obtained, more or less deviating from a straight line; this greatly facilitates the reduction of the figures read off to the true values.

In the adjustment of *apparatus, where mercury is the confining liquid*, which, as a rule, in actual use are placed inversely to their position during calibration, the meniscus correction is carried out as follows:—In the first instance the diameter of the vessel must be ascertained. In some cases, *e.g.* with endiometers, this can be done by direct mensuration. Otherwise, where no special accuracy is required, only the outside diameter is measured, and a deduction of 1 mm. for smaller, or 1·5 mm. for larger widths is made to compensate for the thickness of the glass. The meniscus correction is then calculated for the inside diameter. In doing this, the *double* meniscus correction must be applied, since, as is unavoidable in this case, the apparatus during actual use is placed upside down in comparison with its position during the calibration. This is made clear by Fig. 26, *a* and *b*. During calibration the vessel is in the position *a*, but in actual use in the position *b*. Suppose that in *a* there is 5 c.c. mercury contained in the tube

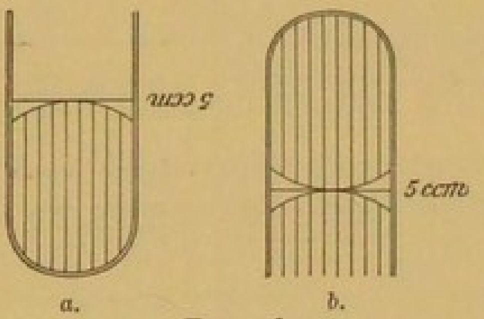


FIG. 26.

up to the mark, there will be in actual use, as shown in *b*, *twice* the difference between the surface of the mercury and the mark.

The following table indicates the double meniscus correction

TABLE VI.—*Double Meniscus Correction for Mercury in Milligrams.*

Diameter.	·0.	·1.	·2.	·3.	·4.	·5.	·6.	·7.	·8.	·9.
mm.										
3	76	70	82	85	88	91	94	97	101	104
4	108	113	118	123	129	135	141	148	156	165
5	174	183	193	204	215	228	243	259	276	294
6	314	336	359	382	406	430	454	478	502	526
7	550	574	598	623	647	671	695	719	744	768
8	792	817	841	866	890	915	940	964	989	1013
9	1038	1063	1088	1113	1138	1163	1188	1213	1238	1263
10	1288	1313	1338	1364	1389	1414	1439	1464	1490	1515
11	1540	1566	1591	1617	1642	1668	1694	1719	1745	1770
12	1796	1822	1848	1874	1900	1926	1953	1979	2005	2031
13	2058	2084	2111	2138	2165	2192	2218	2245	2272	2299
14	2326	2353	2380	2407	2434	2461	2488	2515	2542	2569
15	2596	2624	2651	2679	2706	2734	2762	2789	2817	2844
16	2872	2900	2928	2956	2984	3012	3040	3068	3096	3124
17	3152	3180	3209	3237	3266	3294	3322	3351	3379	3408
18	3436	3465	3494	3522	3551	3580	3608	3637	3666	3695
19	3724	3753	3782	3812	3841	3876	3899	3928	3957	3987
20	4016	4046	4076	4105	4135	4165	4195	4225	4254	4284
21	4314	4344	4374	4404	4434	4464	4494	4524	4554	4584
22	4614	4645	4675	4706	4736	4767	4798	4828	4859	4889
23	4920	4951	4982	5013	5044	5075	5106	5137	5168	5199
24	5230	5261	5293	5324	5356	5387	5418	5450	5481	5513
25	5544	5576	5608	5640	5672	5704	5736	5768	5800	5832
26	5864	5896	5928	5960	5992	6024	6057	6089	6121	6153
27	6185	6218	6251	6284	6317	6350	6383	6416	6449	6482
28	6515	6548	6581	6614	6647	6680	6713	6746	6779	6812
29	6845	6879	6912	6946	6979	7013	7047	7081	7115	7148
30	7182	...	...	...	...	...	...	...	...	...

in milligrams mercury, for tubes from 3 to 30 mm. diameter, progressing by tenths of a millimetre. It holds good for all practically occurring temperatures of a laboratory.

The vessel to be calibrated is fixed in a stand, bottom upwards, so that, *e.g.*, the top-tap of a gas-burette is at the bottom. The outlet-tube of the tap is by means of a strong india-rubber pipe connected with a funnel, and through this at first only so much mercury is run in that it just fills up the bore of the tap, which is then closed, and the elastic tube is removed. Any drops of mercury adhering to the outlet-tube are removed. The apparatus is now placed on the right-hand scale of a balance, or is suspended from this, after having placed the balance on a suitable stand; on the same scale weights are put equal to the weight of mercury corresponding to the entire contents of the vessel, as indicated by the table following below, and the equilibrium is established by placing weights on the left-hand scale. Now the apparatus is again put in the stand, the india-rubber pipe is attached, and mercury is run in up to the lowest mark to be tested, care being taken that the meniscus on rising keeps its proper position. Then the apparatus is again hung below the right-hand scale of the balance, and weights are removed from this until the equilibrium has been re-established.

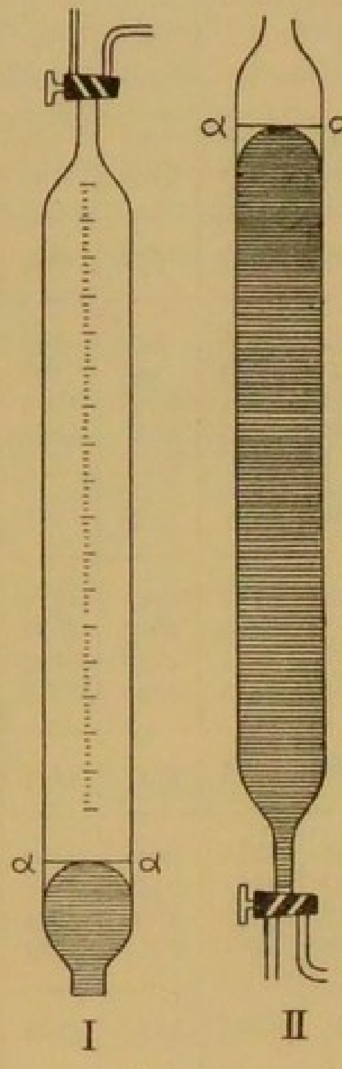


FIG. 27.

Another way of calibrating burettes, etc., for use with mercury is the following, which is adapted to vessels provided with a tap at the top like that shown at I. in Fig. 27 (taken from Treadwell's *Lehrbuch*, ii. p. 610). The vessel, after thorough cleaning, is placed in an inverted, perpendicular position, as shown at II. The capillary of the tap is connected by means of a thick india-rubber tube with a mercury vessel, tap *a* is opened, and mercury is allowed to enter up to a little above the top division. Now the elastic tube and the mercury vessel are removed, and by opening the tap, mercury is run out, until the top of the mercury meniscus just touches the horizontal line *a*—*a* going through the top line (which in the proper position of the burette is the bottom mark) of the division. The parallax fault is avoided, if the reading is made by means of a telescope from a distance of 2 or 3 metres. Now the contents of the tube are run off into a tared flask, which is weighed to 1 cg., the temperature of the mercury is taken, and its volume is found from the following table (drawn up by Schloesser):—

TABLE VII.—*Weights of a Cubic Centimetre of Mercury at Various Temperatures, in Grammes.*

°C.	·0.	·1.	·2.	·3.	·4.	·5.	·6.	·7.	·8.	·9.
15	13·5593	13·5591	13·5589	13·5587	13·5585	13·5583	13·5581	13·5579	13·5577	13·5575
16	573	570	568	566	564	562	560	558	556	554
17	552	550	547	544	543	541	539	537	535	533
18	531	529	527	525	522	520	518	516	514	512
19	510	508	506	504	502	499	497	495	493	491
20	13·5489	13·5487	13·5485	13·5483	13·5481	13·5479	13·5476	13·5474	13·5472	13·5470
21	468	466	464	462	460	458	456	453	451	449
22	447	445	443	441	439	437	435	433	431	429
23	427	424	422	420	418	416	414	412	410	408
24	406	403	401	399	397	395	393	391	389	387
25	13·5385	13·5383	13·5381	13·5378	13·5376	13·5374	13·5372	13·5370	13·5368	13·5366
26	364	362	360	358	355	353	351	349	347	345
27	343	341	339	337	334	332	330	328	326	324
28	322	319	318	316	314	312	310	307	305	303
29	301	299	297	295	293	291	289	287	285	282

Suppose, for instance, that the total contents of the apparatus are = 55 c.c., the normal temperature 15°, the actual temperature of the mercury 19·7°. The measuring-tube of the apparatus is assumed to have shown three different diameters, viz., 7·2, 24·8, and 16·5 mm.; accordingly the meniscus corrections, as shown by Table III., p. 35, are 598 − 548 − 3012 mg. We want to control (*a*) in the narrowest tube the mark 3·0 c.c., in the central part of the apparatus (*b*) the mark 10 c.c., and in the top part (*c*) the mark 50 c.c. We conveniently employ for a tare the weight of 680 grm., equal to that of 50 c.c. mercury. The weight of the apparatus, filled up to those marks, may have been 39·875 for *a*, 272·458 for *b*, 677·025 g. mercury for *c*. In the position for actual use these weights are supposed to have been increased by the meniscus corrections, according to Table VI., p. 43, and would therefore be 40·473 (*a*); 277·939 (*b*); 680·037 (*c*); whereas according to Table VII. on p. 45, they should have been 40·649 (*a*); 270·990 (*b*); 677·476 (*c*). Hence those spaces contain (*a*) 0·176 g. too little; (*b*) 6·949 too much; (*c*) 2·561 too much, which means that the first (*a*) is too little by 0·01 c.c., the second (*b*) too large by 0·51, and the third (*c*) too large by 0·19 c.c.

The examination of apparatus, adjusted for mercury, especially when they are provided with a stopcock, can also be performed by means of water, employing the tables worked out for volumetrical vessels. When doing this, the meniscus of water during calibration is formed in the same position as that of mercury during actual use of the apparatus, as shown in Fig. 28. Since the meniscus of water has a greater volume than that of mercury, the volume tested is found too large by the difference of the *simple* meniscus corrections, water *minus* mercury.

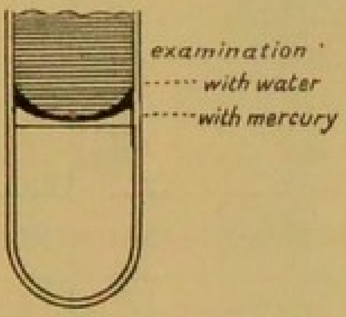


FIG. 28.

These differences are indicated in the subjoined Table VIII., in the column dC_M. If, for instance, in the calibration of a

TABLE VIII.—*Differences of Simple Meniscus Corrections of Water against Mercury, in Cubic Centimetres.*

Diameter. mm.	dC_M.	Diameter. mm.	dC_M.	Diameter. mm.	dC_M	Diameter. mm.	dC_M.
3	3	10	20	17	104	24	247
4	6	11	27	18	123	25	264
5	8	12	36	19	143	26	279
6	10	13	46	20	164	27	293
7	10	14	59	21	187	28	305
8	11	15	72	22	208	29	315
9	15	16	88	23	220	30	424

gas-burette the space marked 20 c.c. had been found = 20·774 c.c. when tested with water, the gas, when employing mercury as confining liquid, would take a space of 20·774 less 0·261 = 20·51 c.c.

Gas-measuring tubes with a millimeter scale, such as Bunsen employs for all purposes, may of course be used for all temperatures and confining liquids, but they must be specially calibrated in each case and used with a corresponding table. Such apparatus is hardly ever employed in *technical* gas-analysis.

The methods and conditions adopted by the *English National Physical Laboratory* for the testing and calibration of glass vessels comprise chiefly apparatus for the volumetric analysis of liquids and solids. We therefore refer to their enumeration in Lunge's *Technical Methods of Chemical Analysis*, translated by C. A. Keane, vol. i. part 1 (1908), pp. 36 *et seq.*

This also holds good of the rules laid down by the *Austrian* Normal-Eichungskommission, quoted in Lunge and Berl's *Chemisch-technische Untersuchungsmethoden*, vol. i. p. 50 (1910)

The rules of the *United States* Bureau of Standards, as quoted by Schloesser in *Z. angew. Chem.* 1908, p. 2168, do not concern us, since there apparatus for gas-analysis is expressly excluded from standardising.

MEASURING IN GAS-METERS.

Extremely important as gas-meters are for their proper purpose, viz., measuring large quantities of coal-gas and other gases, they are but rarely used in gas-analysis, mostly in those cases in which a compound, present in minute proportions, has to be estimated by absorption. The meter is then interposed between the absorbing vessel and an aspirator, *e.g.* a water-jet pump. Hence only that portion of the gas is measured which is not absorbed, whilst the absorbable portion is mostly estimated by titration or gravimetrically.

Gas-meters may also be employed for finding the volume of the bulk of a gaseous current from which an average sample is to be taken.

We distinguish between *wet* and *dry* gas-meters according to whether the gas is measured with or without the aid of a confining liquid. Only wet meters are employed in gas-analysis.

The *wet* or *hydraulic gas-meter* (Figs. 29 and 30) consists of a cylindrical sheet-iron vessel, resting horizontally on a base, filled to a little above half its height with a liquid (water or glycerine of sp. gr. 1·14) in which moves, round a horizontal spindle, a drum divided by diaphragms into several chambers of exactly equal capacity. There are usually four such chambers, all of them provided with an opening near the spindle for the entrance of the gas, and an outlet opening in the periphery of the drum, through which the gas passes into the outer case, and thence into the service pipes. The movement of the drum, caused by the gas passing through, is indicated by a dial arrangement so constructed that it registers both entire and fractional revolutions of the drum. Since the capacity of the drum is known, the volume of the gas passing through can be read off directly upon the dials.

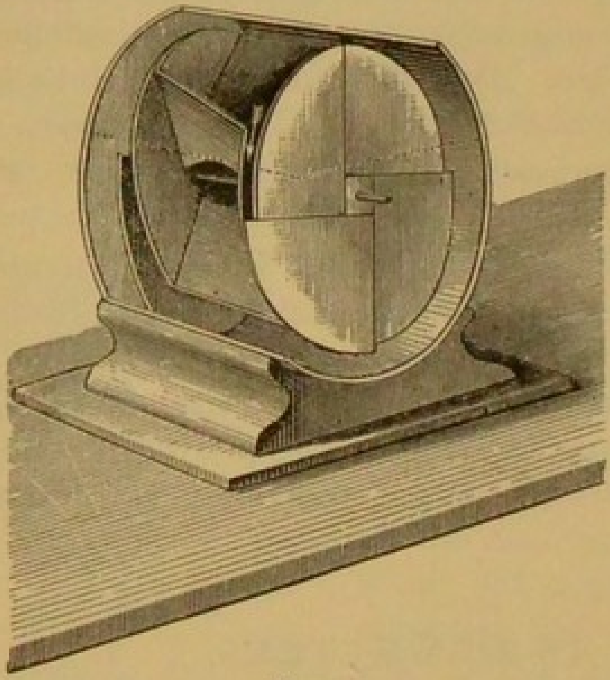


FIG. 29.

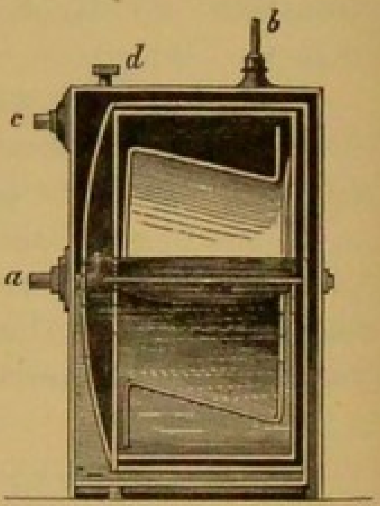


FIG. 30.

The diagrams show a gas-meter in which the luting liquid is filled in by the plug *d*; the gas enters at *a* and goes out through *b*, after having passed through the drum in the direction indicated by an arrow. A second exit is provided by the tap *c*, which is used in case the gas is to be admitted to two sets of pipes at the same time.

For gas-analysis the smallest descriptions of meters, known s "experimental gas-meters," are used, also at the gas-works themselves for photometrical purposes. At the Berlin gas-works these are 36 cm. high, and 33 cm. long; they pass maximum of 500 and a minimum of 10 litres of gas per our. Their indications deviate from the truth *in maximo* by 1 er cent., but the actual error is usually not above 0·1 per cent. Such experimental gas-meters are not officially gauged; but he makers do not send them out if they show greater deviations then ¼ per cent. on passing 200 litres of gas.

Specially constructed experimental gas-meters are sold, *e.g.* by S. Elster, Berlin, by the Rotawerke, Aachen, etc.

Where the same kind of work, consisting in the estimation of the constituent of a gas occurring in minute quantities—*e.g.* ammonia in coal-gas—occurs frequently, it is preferable to perform it always under the same conditions, and therefore to employ the same volume of gas for every estimation. In such cases the outlet of the gas is regulated by means of a tap provided with a micrometer screw. But as the quantity of gas to be employed is usually large and there is considerable time required for passing it through, it is desirable to employ a *gas-meter, which is automatically stopped* after a certain quantity of gas has passed through. Automatic gas-meters have been used in London for official gas-testing purposes ever since about the year 1872. Tieftrunk has described such a meter in which, each time after 100 litres of gas have passed through, the index uncouples a lever, and thus shuts the tap (*Verh. d. Ver. z. Beförd b. Gewerbfl.*, 1876, 5th Appendix).

Gas-meters are never altogether reliable, but they give serviceable approximate indications, especially if merely the number of revolutions is noticed, as shown by the dials, without regarding the absolute volume of the gas passed through. Observations of this kind can be made by means of *gas-meters with arbitrarily divided dials*, as used in physiological laboratories, and supplied by L. A. Riedinger, of Augsburg. These meters pass up to 500 or 600 litres per hour. Their dial is provided with two hands, one of which (the smaller) is fixed to the spindle of the drum and moves along with it, indicating the smaller divisions. This hand makes 100 revolutions before the second (larger) hand has completed one. The drum holds 25 litres, corresponding to one revolution of the smaller, or $\frac{1}{100}$ of a revolution of the larger hand. The dials are arranged in such manner that 2 c.c. can be read off with certainty.

Every gas-meter should be tested by *gauging*. This can be done by passing through it varying quantities of air at a constant temperature by means of a large aspirator, provided with a pressure gauge, and collecting the water running out in litre-flasks. The volume of this water is equal to that of the air employed, if the pressure gauge indicates an equilibrium both at the beginning and at the end of the experiment.

Julius Pintsch, A. G. (Ger. P. 247871) describes a gas-meter intended for measuring gases under variable and high pressures.

APPARATUS FOR MEASURING THE VOLUME OF GAS WHILE PASSING THROUGH TUBES.

The "Rotameter" of the Deutsche Rotawerke, Aachen, allows of directly reading off the quantity of a gas (or liquid) passing through per hour. It consists of a glass tube, wider in the top part, and provided with a scale for litres per hour. The gas entering from below causes a float, provided with steeply ascending channels, to revolve quickly round its vertical axis, and the position of this float immediately indicates the litres of gas passing through per hour. This float revolves freely and visibly, without touching the walls of the pipe, so that no errors are caused by friction.

Ubbelohde and Hofsäes (*Z. f. Elektrochem.*, 1913, xix. p. 32), by the name of "Capometer," describe a contrivance for the same purpose, also a viscosimeter (sold by C. Desaga, Heidelberg).

Nicolardet (*Ann. Chim. anal. appl.*, 1913, p. 136; *Z. angew. Chem.*, 1914, II. p. 9) describes an apparatus for measuring the volume of gases which are very little soluble in water, and which do not act upon mercury.

VARIOUS APPARATUS FOR GAS-ANALYSIS.

These apparatus are of two different descriptions. Either they serve both for absorbing and measuring purposes, or the measuring-tube is separated from the absorbing arrangements.

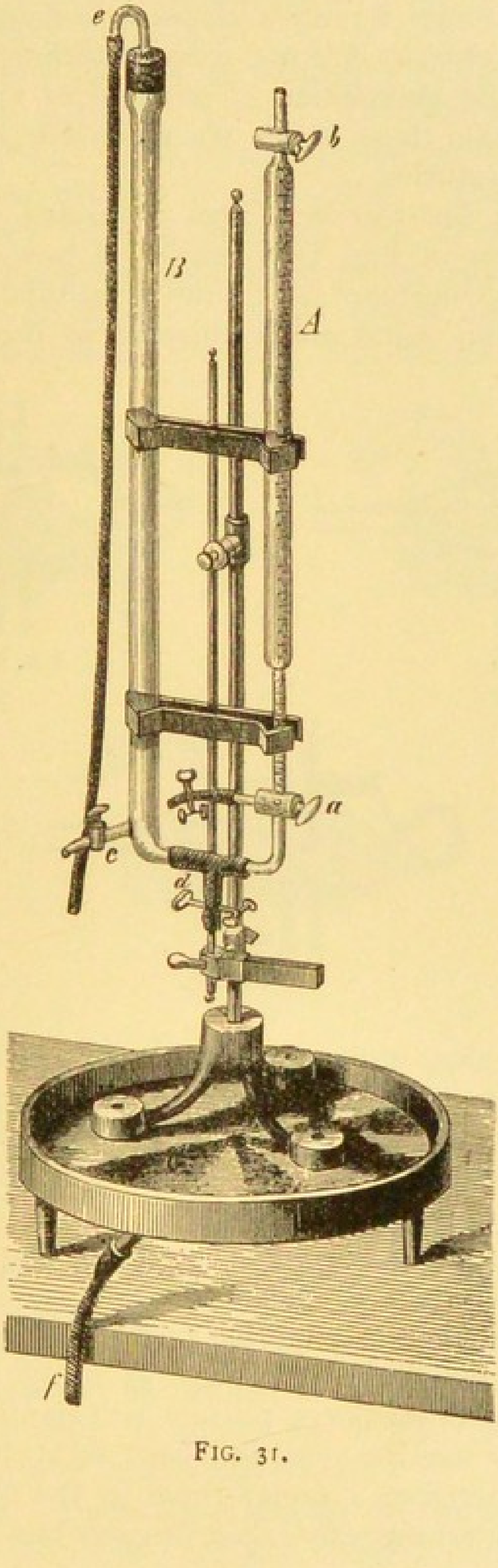


FIG. 31.

A. *Apparatus for absorbing and measuring in the Same Tube.*—To this class belongs Bunsen's classical eudiometer, which we do not describe here, as it is not used in technical gas-analysis. We also omit the description of most older apparatus of this class, but we retain those which are up to the present found in very many laboratories.

1. *Winkler's Gas-Burette.*—This apparatus, constructed in 1872, and shown in Fig. 31, consists of two communicating tubes, the measuring-tube A and the level tube B, held by the clamps of an iron stand, and connected at the bottom by an india-rubber T-piece *d*, the free branch of which is closed by a pinchcock. Tube A serves for receiving the gas, and is at its bottom provided with a double-bored side-tap *a*, of peculiar construction. Its shape, as originally designed by Winkler, is shown in Figs. 32 to 34.

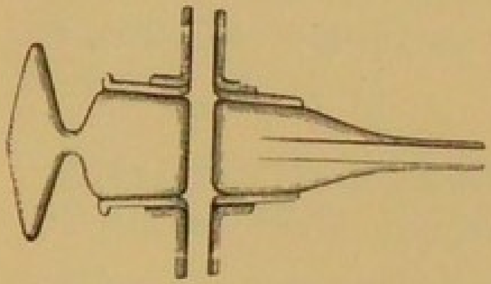


FIG. 32.

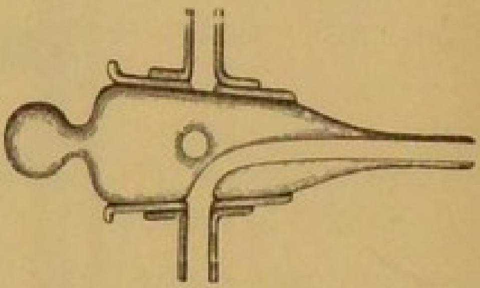


FIG. 33.

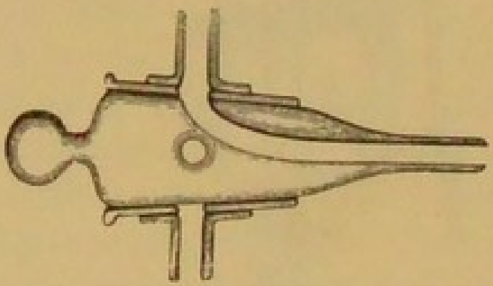


FIG. 34.

The tap possesses an axial bore, curving sideways, and issuing at right angles to the others, an ordinary cross bore. Another kind of three-way tap has been constructed by Greiner and Friedrichs, and is shown in Figs. 35 to 37. These, instead of the axial and cross bores, possess two slanting bores; they are more easily manipulated and kept tight than the former construction, wherefore I prefer them to the original Winkler taps (sometimes erroneously called Geissler taps) for the various apparatus constructed by myself (cf. *Z. anal. Chem.*, 1887, p. 49 and *Berl. Ber.*, 1888, xxi. p. 376).

The measuring-tube A of Winkler's gas-burette, Fig. 31, is closed at the top by a tap *b*. Between taps *a* and *b* it holds about 100 c.c. It is exactly measured once for all, and the contents are marked on the tube. This is, moreover, divided from the bottom upwards into tenths of a cubic centimetre, including the contracted pieces adjoining the taps. The lower one of these contracted pieces occupies about a quarter of the length of the tube, and serves for measuring small volumes; the upper one should be as short as possible, so as to prevent any liquid from adhering to it.

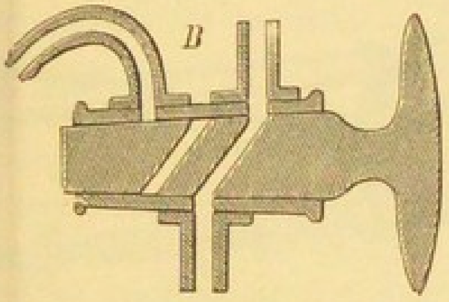


FIG. 35.

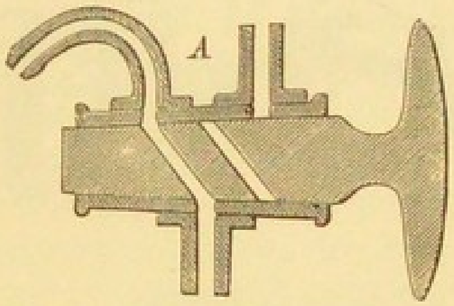


FIG. 36.

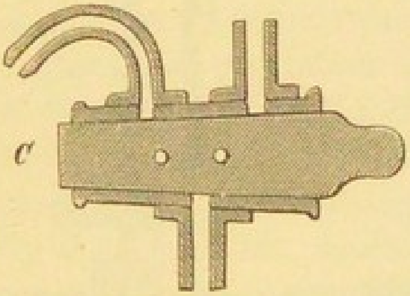


FIG. 37.

The level tube B receives the absorbing liquid. It is closed at the top by an india-rubber stopper, through which passes the bent tube *e*, with an elastic tube attached to it. The lateral outlet-tap *c*, which increases the chance of a fracture, is not indispensable and may be left out.

The stand carries a movable holder for the tubes, so that these may be placed at will either in a vertical or a horizontal position. The burette is placed on a lead lined basin *c*, to receive the absorbing liquids and rinsings.

Manipulation.—Open tap *b*, and by means of tap *a*, and of an india-rubber pump or aspirator, cause a current of the gas to be analysed to pass through tube A, until all air has been driven out. According to whether this is done by pressure or by aspiration, either tap *a* or tap *b* is closed first, in order to have

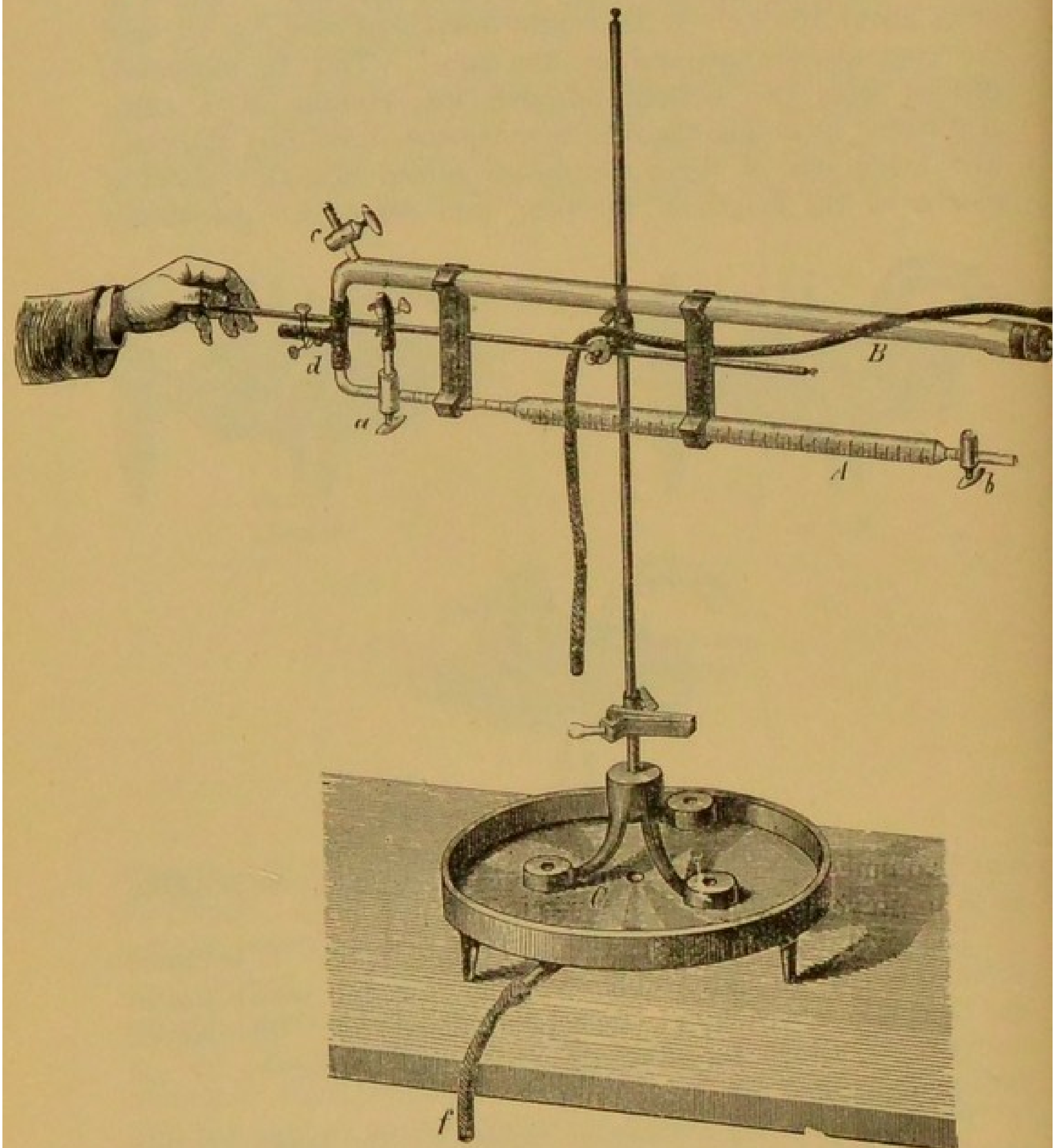


FIG. 38.

the gas under the pressure of the outside atmosphere. Tap *a* is put in such a position that the inner end of its longitudinal bore is turned outwards.

The level tube B is now filled with the absorbing liquid. The air enclosed below tap *a* is expelled by a momentary opening of the pinchcock attached to that tap. Thus the gas and the liquid are only separated by tap *a*. To start the absorbing process, the plug of *a* is turned so as to make a connection between A and B. The absorbing liquid now begins to enter into A; by blowing into the india-rubber tube attached to B, the liquid is forced up a little in A, and tap *a* is closed again. By alternately placing the tubes horizontally as shown in Fig. 38, and vertically, the gas and the liquid are brought into intimate contact, and the liquid quickly absorbs that portion of the gas for which it is intended. If, on opening tap *a*, no more liquid enters into A, the absorption is complete. We must now cause the liquid to assume the same level in A and B, either by opening the lateral tap *c* or by the pinchcock *d*, leaving tap *a* open in the meanwhile. The volume of the liquid now contained in A is equal to that of the gas absorbed, and is converted into per cent. by volume by multiplication with 100 and division by the total number of cubic centimetres that tube holds.

After every estimation the apparatus is thoroughly rinsed with water; the taps are dried with blotting paper, and the plugs are again slightly greased all over. During the time the apparatus is out of use, the plugs of the taps are better taken out, as they frequently stick very fast when left in.

Winkler's gas-burette is principally applied for estimating carbon dioxide in gases from chimneys, blast-furnaces, lime-kilns, etc., by means of a moderately strong solution of caustic potash, and for estimating oxygen in atmospheric air, etc., by an alkaline solution of pyrogallol.

2. *A. Lange's modification of the Winkler gas-burette* is intended for the examination of *liquid carbon dioxide*, or *chlorine*, and of *natural sources of gaseous carbon dioxide*. It is shown in Fig. 39. Tube A, holding 100 c.c., is at the top contracted into a tube holding 5 c.c., graduated into 0·05 c.c. A is connected by an india-rubber pipe with tube B, from the top of which, at *c*, descends an india-rubber pipe, ending in a glass tube which dips into the 250 c.c. bottle D, fixed on the same stand. Caustic soda solution of sp. gr. 1·297 is poured into B, until both B and A are filled rather more than half-way

up. The cork, with tube *c* and the elastic tube, is put on B, and by means of another elastic tube, put on *b*, air is blown into A, until the level of the liquid is below tap *a*, which is then closed.

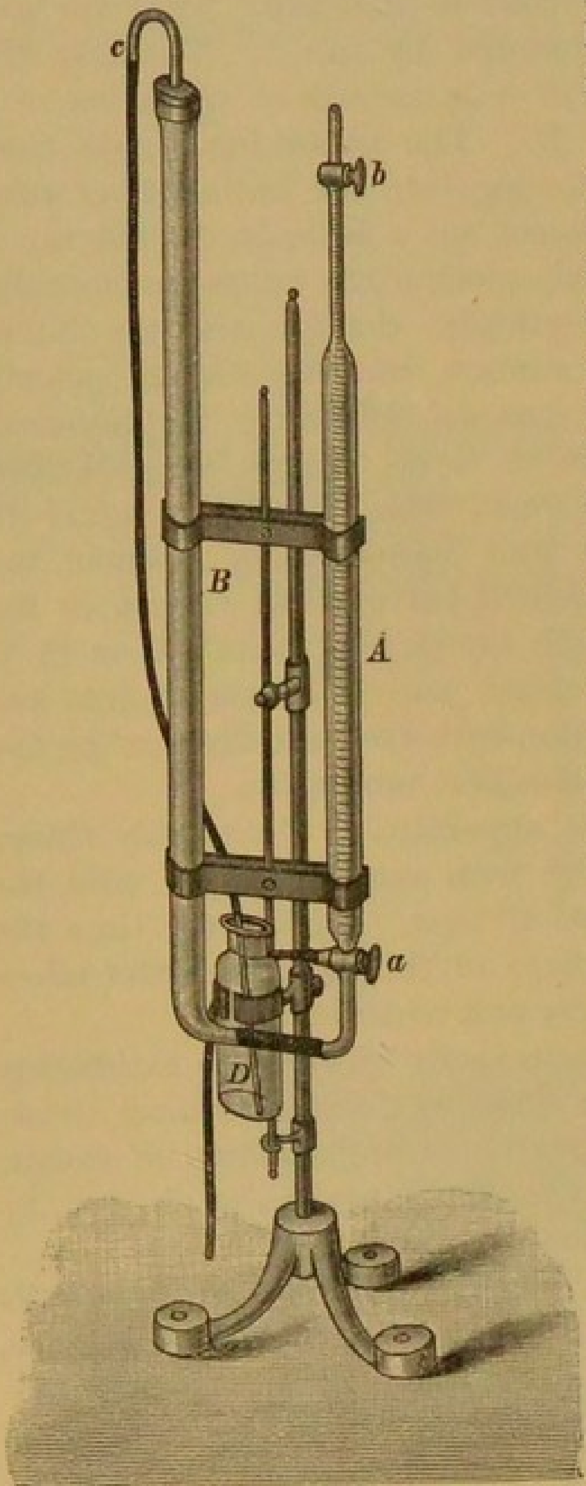


FIG. 39.

Now B is filled with the same solution, as well as *c*, the elastic tube, and D; by opening tap *b* it is ascertained that the bore of this tap is also filled, and the apparatus is now ready for use. By turning the three-way tap *a* ninety degrees, the gas is passed into A, until it issues at *b*. When *b* is closed and *a* opened, the potash solution, owing to the absorption of CO_2, will get from D into B and A. After the absorption has been finished, *b* is opened; the potash solution flows back into D, and the level is automatically restored in the tubes, and the apparatus is again ready for use. Upwards of four hundred tests can be made without renewing the potash solution.

In order to test *liquid carbon dioxide*, the iron bottle containing it is placed in an upright position; a coupling-piece is tightly screwed on, and an elastic tube is drawn over its free end. The valve of the bottle is now cautiously opened and is regulated so as to yield a regular, moderate stream of gaseous carbon dioxide. Now the elastic tube is slipped over tap *a*, which is turned so as to admit the carbon dioxide nto A; the air from this escapes through the open tap *b*. After one minute A is filled with carbon dioxide, and this gas is passed through, until needle-shaped crystals of potassium hydrocarbonate appear in the contracted part of A. Then *b* is closed, the elastic tube is taken off, whereupon the pressure within A becomes equal to that of the outer air, and *a* is turned 90°, so that A communicates with B. The potash liquor at once rises in A, and by inclining the apparatus ultimately to the horizontal, the absorption in A is accelerated without the formation of a vacuum. The absorption is completed by moving the apparatus upwards and downwards; it is then fixed in the vertical position, bottle D is lifted up until the levels in A and D are in the same plane, and the volume of gas in A is read off. Two such tests should not differ by more than 0·05 per cent. As the divisions on the contracted part of A indicate 0·05 c.c., readings can be made to 0·01 c.c.

In order to take a sample of the liquid carbon dioxide contained in an iron bottle, this is placed horizontally on a stool, so that the coupling-joint of the valve points upwards. By slowly opening the valve, it is generally possible to produce a convenient, moderate stream of CO_2, but small quantities of solid CO_2 are always ejected. In some cases the adjustment of the stream is very troublesome; it issues in jerks and sometimes stops, but on touching the valve ever so slightly it becomes so violent that the elastic tubes are thrown off. In such cases a reducing-valve must be interposed, but the gas must be allowed to issue long enough to drive out all the air from the valves; in this case the results agree completely with those obtained directly from the contents of the bottle.

In order to examine *liquid chlorine* and *strong chlorine gas*, or the *carbon dioxide in electrolytic chlorine*, the process is carried out as just described; but the absorbent employed is a concentrated solution of ferrous chloride, which absorbs the chlorine rapidly and in quantity, leaving air and carbon dioxide behind. Another sample of the gas is treated in a second burette with caustic potash solution which absorbs the chlorine and carbon dioxide, leaving only the air as gaseous residue. The CO_2 is found by the difference of these two tests. It would be probably best first to saturate the ferrous chloride solution with carbon dioxide.

3. *Honigmann's gas-burette*, Fig. 40, consists of a measuring-tube A, closed at the top by tap *a*; the bottom end *b* is left open, and is connected with a stout india-rubber tube. The burette contains exactly 100 c.c. from a zero mark near the bottom up to the top; it is graduated into fifth parts of a cubic centimetre. The absorbing liquid is contained in the glass jar C, into which A can be plunged down to any depth.

FIG. 40.

This burette is specially intended for estimating the percentage of carbon dioxide in the gases employed for carbonating the ammoniacal solution of sodium chloride in the ammonia soda process, but it serves also for testing lime-kiln gases and other gaseous mixtures containing CO_2. The gas to be tested is drawn through A, until all air has been expelled; tap *a* is closed, and A is immersed in C, which has been previously filled with a solution of caustic potash, exactly to the zero mark on A. Tap *a* is now opened for a moment, in order to equalise the pressure within and without, whereupon exactly 100 c.c. of gas is contained in the burette. The absorption of CO_2 is started by immersing A a little lower, so that its inside is wetted by the potash solution, and then putting it out but leaving the end of the elastic tube within the liquid; A can thus be moved about and downwards. The potash solution enters into it as the CO_2 is getting absorbed, and the absorption is soon completed. Now A is again immersed in C, until the levels inside and outside are the same, and the reading is taken which indicates directly the percentage of CO_2 by volume. This apparatus cannot, of course, yield very accurate results, but its construction and manipulation are very simple, and each test takes only a few minutes. Both the burette and the elastic tube must be carefully rinsed with water after each test.

4. *The Bunte Burette.*—This, one of the most useful and widely used apparatus for technical gas-analysis, was first

escribed in the *J. Gasbeleucht.*, 1877, p. 447, and *Dingl. olyt. J.*, ccxxviii., 1878, p. 229. It is an improvement of a as-burette described by Raoult in *Comptes rend.*, lxxxii. p. 844 876). It is shown in Fig. 41.

The measuring-tube A is at the top closed by a three-way lass tap *a*, preferably of the Greiner-Friedrichs shape (*suprà*, . 52), surmounted by a funnel *t*, and at the bottom closed by the lain glass tap *b*. The space between taps *a* and *b* is rather more han 110 c.c., and is divided into fifths of a cubic centimetre. he mark 100 coincides with the capillary of the upper tap *a* this capillary remains filled with water and is therefore not ncluded); the zero mark is 6 or 8 c.c. above the tap *b*, and he division is carried 10 c.c. below this. The gas in this urette is always measured at the atmospheric pressure, plus he pressure of the column of water contained in the funnel *t* p to the mark. The burette was formerly provided with a lass jacket to prevent cooling, but this was left off later on as eing unnecessary in an ordinary laboratory.

This tube is fixed to an iron stand by means of an easily pened clamp. A second arm on this stand carries the funnel B, which can be connected by an india-rubber tube, about 3 mm. wide, with the capillary bottom end of the burette.

To the apparatus belong further a small glass or porcelain up C for holding the absorbing liquids, and two aspirating ottles, D and E, of the shape shown in the diagram. Bottle D erves for forcing water into the burette, or withdrawing it therefrom. In both cases the rubber end *n* is put upon the bottom apillary *b*; and air is during this operation blown by the mouth nto the tube *m*, so that, during the fixing of the tube on *b*, water is always running out of *n*, and no air-bubble can get in. This precaution must *never* be omitted. If larger quantities of iquid are to be withdrawn from the burette, the bottle E is employed; it is attached directly to the burette, the air having been evacuated from it by means of a water-jet pump.

By permission of Professor Bunte, we take the following points from his instructions "Zum Gaskursus," printed in 1906 as manuscript" for the use of his students in gas-analysis.

Bunte burettes, in order to properly fulfil their purpose, must answer to the following conditions:—The capillary below the bottom tap *b* must not allow any water to flow out, even on

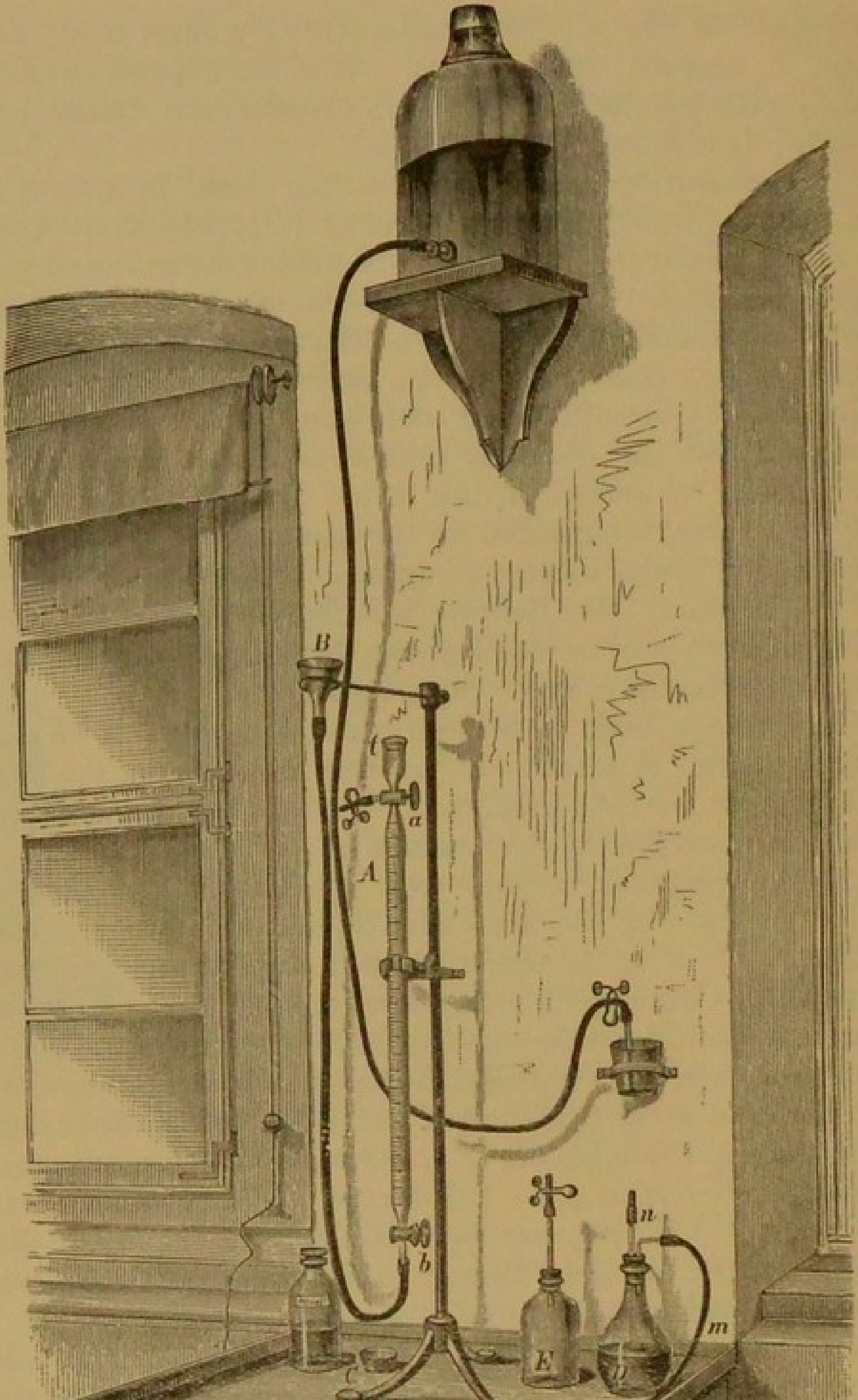


FIG. 41.

aking the burette. The three-way tap at the top (*a*) must be constructed that all its three bores can be closed (this is ite easy in the case of Greiner-Friedrichs taps). The taps ust be greased with a fused mixture of 2 parts Para-caoutchouc, parts beeswax, and 10 parts tallow, or a mixture of vaseline nd Para-caoutchouc. They must close perfectly tightly even gainst a strong vacuum. The confining water must have xactly the same temperature as the working-room, and this ust remain perfectly constant during the analysis. The urette must be touched for handling only at the top funnel (*t*) r at the capillary branches. The marking is to be controlled y running out the water from 2 to 10 c.c. (*vide suprà*, pp. 36, *seq.*). After the absorption of a gas, first water is allowed to nter from below, and then the working pressure is established y allowing water to run down from the upper funnel (*t*); this nnel is filled up to the mark, the upper tap (*a*) is opened, aiting for one minute until the surface of the water in the urette does not rise any more.

The gas to be tested is introduced into the burette either hen this is empty (the funnel *t* being full) by passing the as through until all the air has been driven out, then shutting rst the bottom tap *b* and immediately afterwards the top ap *a*; or else after filling the burette with water, by opening oth taps, until the water has sunk about 1 c.c. below the zero ark, and then closing first the upper, after this the lower tap. f the gas to be sampled is under low pressure, a sample of it ust be taken by means of an india-rubber pump, or an spirating bottle, or a water-jet pump, connected with the ottom capillary.

It is hardly necessary to say that before introducing a fresh ample of gas into the burette, this must be most thoroughly leaned. If, *e.g.*, it is merely employed for estimating carbon ioxide, and any alkaline liquid were left adhering to the glass efore introducing the new gas-sample (a fault not infrequently ommitted in works' laboratories), too little CO_2 would be ound in the fresh sample, because some of it would be taken ut by the adhering liquid before measuring the gas.

The ordinary manipulation is as follows:—Water is run nto the burette through the funnel B, until it begins to enter nto the top funnel *t*. The taps are now closed, and the india-rubber tube is detached from the bottom of the burette. The three-way tap *a* is now turned so that the burette communicates with the tube conveying the gas, which tube is already filled with the same, and the gas is drawn into the burette by running water out of the bottom tap *b*. Rather more than 100 c.c., say 100·5 c.c., of gas is allowed to enter the burette, tap *b* is turned so that all its openings are closed, and the exact adjustment to the zero mark is made as follows:—By means of the bottle D sufficient water is forced into the burette to compress the gas to about 95 c.c.; then *b* is closed, the bottle D is taken off, and by cautiously turning the tap *b* the water is run out again, exactly to the zero mark. The gas is still under a plus pressure, and now, by a last operation, that pressure has to be established at which every reading has to take place. For this purpose the funnel *t* is filled with water up to the mark, and tap *a* is opened for an instant, which causes the excess of gas to escape through the water in *t*. The burette ought now to contain exactly 100 c.c. of gas at the pressure of the atmosphere, plus the pressure of the column of water standing in the funnel *t*. If the water is not exactly at the zero mark, its level is read off and the calculations made on the real volume of the gas.

Now a little water is run out of the funnel *t* by means of the three-way tap *a*, into a short bit of india-rubber tube, which is then closed by a glass rod; this remains as long as the tap is not used.

The absorbing liquids are introduced in the following way:—The water contained in the burette is drawn off by means of the bottle D down to the tap *b*, which is held fast and is immediately closed as soon as the water has gone down to the capillary part. The end of the burette is now dipped into the cup C, which has been charged with the absorbing liquid. If tap *b* is now opened, a volume of the absorbing liquid, almost equal to that of the water drawn off, enters the burette and rises in it almost up to the zero point, but not quite, owing to its higher specific gravity. In any case the quantity of liquid thus introduced suffices for removing the absorbable constituent of the gas, and in order to effect this it is only necessary to bring the gas and the liquid into intimate contact. For this purpose the burette, after closing the tap *b*, is taken hold of by he upper capillary between the first finger and the thumb, losing the funnel top by the hand, and the burette is moved p and down in short, but not violent jerks. When the bsorption is complete, the bottom end of the burette is again lipped into the cup C, and tap *b* is opened, whereupon liquid nters in the place of the absorbed gas. If, on repeating the ust-described operations the liquid within the burette remains t the same level, the reading may be taken. First, however, he gas has to be put under the proper pressure by running vater into the burette out of the funnel *t* (whereby also the nside of the burette is rinsed) and filling *t* with water up to he mark.

Since the adhesion of the absorbing liquids differs from that f water, it is preferable to remove those liquids by water and o repeat the reading. For this purpose both taps *a* and *b* re opened, water being run into funnel *t* in a steady stream, nd thus the burette is rinsed until the liquid running out is ure water. No gas is lost in this way, and therefore after he water contained in the burette has been drawn off in the bove-described way, a different reagent can be introduced n order to absorb another of the gaseous constituents. In the ame way a third and fourth gaseous constituent can be emoved, and its volume determined by rinsing out and introlucing suitable absorbents. But as this manipulation requires he use of a large quantity of water, by which some of the gas nay be dissolved, it is preferable to draw off most of the bsorbing liquid by suction and wash the burette by means of few cubic centimetres of water, which is again sucked off, epeating this as often as may be necessary.

We shall further illustrate the manipulation of the Bunte urette by describing a determination of carbon dioxide say in oal-gas. For this 1 c.c. of caustic potash solution is introduced n the way described on p. 62. After closing tap *b*, the burette s taken out of the clamp, taking hold of it with the thumb and irst finger of the right hand at the capillary below the upper ap *a*, and it is inclined in such manner that the whole of its nside gets wetted by the caustic liquor, or else jerked as lescribed *suprà*. The absorption of the CO_2 is almost instantaneous. The burette is put back into the clamp, the liquor is allowed a minute or so to run down, water is again poured into the top funnel *t*, and by suitably turning tap *a*, about 1 c.c. of water is run into the burette, whereby the caustic liquor is washed off the glass. The liquor at the bottom is drawn out by means of the aspirating bottle D, and the washing of the burette is repeated with 1 or 2 c.c. of water. The volume of gas left in the burette must now be read off. For this purpose water is introduced by means of funnel B, the elastic tube of which is put on the bottom outlet with the above-described precautions against any air getting in. When no more water enters into the burette tap *b* is closed. The gas in A is now under plus-pressure. The elastic tube is taken away, and water is run out of tap *b* as much as will do so of its own accord. The gas is now under minus-pressure. If, therefore, tap *a* is opened so that A communicates with funnel *t*, some water runs out of this into A, and is replaced by other water up to mark on *t*, whereby the gas now contained in the burette is under the same conditions of pressure as on measuring off the original gas. After closing tap *a*, a minute is allowed for the water to run off the inside surface of A, and the volume in A is read off.

The Bunte burette can be employed for most gas-analytical operations, either by itself or in connection with other apparatus. Some of its principal applications are:—

1*st*. For the estimation of carbon dioxide in mixtures of that gas with air, or fire-gases, gases from blast-furnaces, lime-kilns, gas-producers, and so forth, by means of potassium hydrate solution.

2*nd*. For the estimation of oxygen, either by itself (as in atmospheric air) or when mixed with carbon dioxide, nitrogen, and other gases. If CO_2 is present this is in any case taken out by potash solution, and the oxygen afterwards absorbed by a strongly alkaline solution of pyrogallol.

3*rd*. For the estimation of carbon monoxide by means of absorption in a solution of cuprous chloride in hydrochloric acid. Before doing so any carbon dioxide and oxygen must be taken out first, whether they are to be estimated or not.

4*th*. For the estimation of hydrocarbons, of hydrogen, of methane, etc., as will be described later on in connection with the analysis of coal-gas.

For some of these purposes the Bunte burette must be combined with apparatus for fractional combustion, or provided with platinum points for producing an explosion by means of the electric spark. These arrangements will be described later on when treating of the methods in question.

Various modifications of the Bunte burette have been proposed—*e.g.* by Francke, Schuhmacher, Pfeiffer—but these need not be described in this place. A modification, particularly arranged for working with sulphuretted hydrogen, is described in the 49*th Report of the Alkali Inspectors for the year* 1912, pp. 20 *et seq.*

B.—APPARATUS PROVIDED WITH ABSORBING PARTS SEPARATED FROM THE MEASURING-TUBE.

The just-described Bunte burette in some of its applications belongs already to this class, as is made clear in describing it. In this kind of apparatus the absorption of a gaseous constituent is not carried out in the measuring-tube itself, but in a separate vessel which serves for holding the absorbing liquid, and for bringing the gas into contact with it after being measured. When the absorption has been finished, the remaining gas is again transferred to the measuring-tube where its volume is read off. The volume of the gas taken out by the absorbing reagent follows from the difference of the two readings.

This way of proceeding admits of thoroughly utilising the absorbent, and dispenses with washing out the measuring-tube after each estimation. In this way hundreds of measurings can be carried out without necessitating any intermediate operation, and before changing and refilling the apparatus. Hence such apparatus are eminently adapted for technical purposes, especially for the regular control of technical operations.

The measuring and absorbing vessels must be capable of being connected with each other either in a temporary or a permanent way. The connection is usually made by a narrow capillary tube whose contents scarcely amount to 0·1 c.c.; hence the quantity of air contained in it, which gets mixed with the gas to be examined, is so slight that it does not sensibly influence the result. In special cases this capillary tube may be filled with water in order to avoid that slight admixture with air.

The first apparatus of this class was that constructed by Scheibler for estimating the carbon dioxide in the saturation gases of sugar works. This apparatus, like some others, did very good service in its time, but has been superseded by others of a simpler or more efficient description, which we shall now enumerate.

ORSAT'S APPARATUS.

The apparatus now generally known by this name and used in thousands of factories has not been first proposed by Orsat, but by Regnault and Reiset, in 1853, for scientific purposes. Its first application for technical purposes is due to Schlösing and Rolland, in 1868 (*Ann. Chim. Phys.* (iv.) xiv. p. 55), who gave it already the form now generally used; it was improved by Orsat in 1875 (*Ann. des Mines* (vii.) viii. pp. 485, 501), and later on by Salleron, Aron, Ferd. Fischer, Muencke, Lunge, and various others.

We show in Fig. 42 the "Orsat" as modified by F. Fischer. The measuring-tube or burette A contains exactly 100 c.c. from the zero mark near its bottom to the capillary end at the top. The narrower portion of the measuring-tube is divided into tenths of a cubic centimetre. The burette A is surrounded by a water-jacket, in order to protect it against the influence of changes of the outer temperature during the operation. This water-jacket is closed at top and bottom by india-rubber stoppers, and is sometimes provided with a white background of opaque glass, on which the black divisions of the burette are more plainly visible. The burette ends at top and bottom in thick capillary tubes which fit into suitable projections of the wooden frame. The bottom end is connected by an india-rubber tube with a pressure bottle L, filled two-thirds with water; the top is connected with a glass capillary, bent at a right angle and ending in the three-way cock *c*, which allows of connection with the gas supply and the tube B, or between B and A, or between A and the outside air. The horizontal capillary is provided with two capillary branches, which are continued into glass taps *n* and *m*, with a mark on each of them below the tap, which at their capillary bottom ends are connected by india-rubber joints with the U-shaped absorption vessels, D and E, usually called "pipettes." The horizontal capillary tube is at its end bent down and connected with a U-tube B, filled with cotton-wool, in order to retain all soot and dust contained in the gas sample.

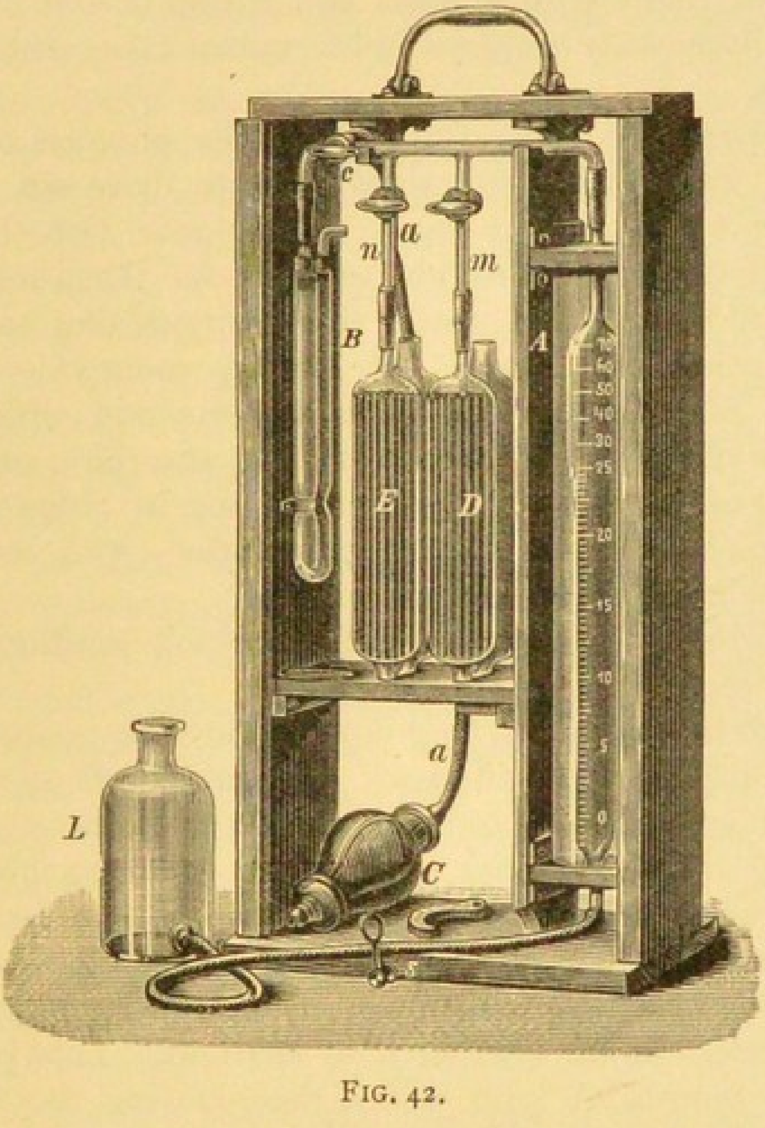


FIG. 42.

The "pipettes" D and E are filled with bundles of glass tubes, so as to provide a large surface of contact between the gas and the absorbent; the open end of each pipette is closed by a rubber stopper to which a thin rubber ball is attached, the object of which is to protect the contained liquids from contact with the air.

The mark in the capillary end of the glass taps *n* and *m* being above the joint with the pipettes, this joint is always wetted inside by water and is therefore easily kept tight.

Since these glass taps sometimes stick fast and are then easily broken in trying to open them (this ought not to happen if they are properly greased with vaseline or other suitable substances, as is anyhow necessary, *cf.* p. 15), Naef recommends in lieu of them the so-called Bunsen valves, *i.e.*, india-rubber tubes with a glass ball inside (*Chem. Ind.*, 1885, p. 289). Olschewsky employs india-rubber tubes with ordinary pinchcocks.

To prepare the apparatus for use, the pressure bottle L is filled with water and then raised so as to drive out the air in the burette A through the tap *c*. The pipette D is then filled, say, with potassium hydroxide solution for the absorption of carbon dioxide, and the pipette E with pyrogallol solution for the absorption of oxygen. If carbon monoxide is to be estimated as well, the apparatus is provided with a third capillary branch glass tap and a special absorbing pipette, the glass tubes of which contain copper spirals, in order to protect the ammoniacal cuprous chloride solution with which this pipette is filled against oxidation.

The method of preparing the absorbing solutions will be described later on.

To introduce the absorbing liquids, they are poured into the respective pipette from the back, after taking off its stopper so as to fill about half of it, and then drawn up to the mark *m* or *n* by opening the tap of that pipette and lowering the pressure bottle L; when the liquid reaches the mark, the tap is closed and the rubber ball inserted at the back of the pipette.

Before proceeding with an analysis, the apparatus should first be tested to see whether it is air-tight. This is done by filling the burette A with water, then closing the tap *c*, and lowering the pressure bottle L, when it will at once be seen from any change in level of the water in A, whether there is any leakage.

In order to introduce the sample of gas, A is again filled with water, the tap *c* turned so as to communicate with B and the outside air and the rubber aspirator C, which is connected with the gas supply, and then attached to the exit-tube of B. After clearing out the air in B by aspirating, the tap *c* is turned so as to connect the gas supply with the burette A, and the sample introduced by lowering the pressure bottle L. A little more than 100 c.c. is syphoned into A, and the tap *c* is then closed. To obtain exactly 100 c.c. for analysis, the gas is compressed to the zero mark by raising L; the rubber tube *s* between L and A is then closed either by the pinchcock or by the fingers, and the tap *c* momentarily opened to the outside air, so as to establish the atmospheric pressure on the contained gas.

Before introducing the gas into A, care must be taken to completely remove the air contained in the tubes connected with the chimney, gas-flue, or other place whence the gas is to be taken. This is done by turning tap *c* so as to connect the rubber aspirator C′ with the source of the gas, and compressing and loosening C′ ten or twelve times, whereupon the connecting tube is sure to be filled with the gas to be examined.

Suppose we want now to determine the *carbon dioxide.* We open the tap *m* and transfer the gas from the burette A into the pipette D, by raising the pressure bottle L with the left hand, so that, on opening the pinchcock *s* by the right hand, gas enters into D. Now L is again lowered, until the caustic liquor in D rises about to the rubber junction below *m*, and the gas is once more driven into D by raising L.

This operation is repeated several times, by alternately lowering and raising L, until the absorption is complete. Finally, the level of the liquid in D is brought up to the mark *m*, the attached tap closed and the reading in the burette taken, the pressure of the gas in A being adjusted to that of the atmosphere by raising L, so that the height of the liquid in L and that in the burette is the same. The reading obtained gives the percentage of CO_2 directly.

Precisely in the same way the gas is now two or three times passed into the pyrogallol pipette E until no further absorption takes place, and the remaining gas again transferred into A. The diminution of the volume of gas against the last reading indicates the percentage of *oxygen.*

If, as is a very usual case, any *carbon monoxide* present in the sample is to be determined, the apparatus is for this purpose provided with a third pipette, charged with an ammoniacal solution of cuprous chloride, as mentioned *suprà*,

p. 64. The preparation of this solution will be described later on. As it becomes unreliable after some time, Fischer prefers to omit this determination in the analysis of furnace-gases, but in that of producer-gases and similar cases the carbon monoxide is just one of the principal constituents of the gas, and must be determined in one way or another.

When the analysis is completed, the residual gas is cleared out of the burette A, and the apparatus is again ready for use. The estimation of CO_2 and O can be completed in five minutes, with an accuracy of 0·2 per cent. The estimation of CO takes rather more time, as we shall see later on.

When the absorption after prolonged use of the apparatus is becoming too slow, the contents of the pipettes getting exhausted, they are removed by means of a small syphon, and the pipettes are thoroughly washed out with distilled water before introducing a fresh charge of the absorbent. In case any of the absorbing liquid should have got into the capillary tube above the stopcocks of the pipettes, the tubes should be thoroughly washed out with water through the tap *c*, the other taps being shut, and the water in A and L renewed. It is important to grease all the stopcocks before the apparatus is put aside after use.

In order to save the trouble of repeatedly transferring the gas from the burette into the absorbing pipettes and back, several automatically acting apparatus have been constructed, *e.g.*, by Namias (*Stahl u. Eisen*, 1896, p. 788); Le Docte (*Chem. Zeit.*, 1900, p. 375); Cario (Ger. P. 98667; *Chem. Zeit.*, 1898, p. 977).

L. Kaufmann & Co. (*Chem. Zeit. Rep.*, 1901, p. 26) describe, by the name of "Ados," an apparatus for automatically analysing furnace gases and continually registering the results. L. M. Dennis (*Gas-Analysis*, 1913, pp. 85 *et seq.*) describes an improved form of the Orsat apparatus.

The absorbing solutions usually employed are the following:—

1. For absorbing carbon dioxide: a solution of potassium hydroxide of sp. gr. 1·25. Caustic soda solutions are not to be recommended, as they act more strongly upon the glass, and as the sodium carbonate formed crystallises out.

2. For absorbing oxygen: the same solution of potassium

hydroxide in which 15 to 25 g. of pyrogallol are dissolved for each apparatus.

In lieu of this reagent, some prefer very thin sticks of phosphorus, the pipette being filled up with water, but containing no glass tubes.

3. For absorbing carbon monoxide: an ammoniacal solution of cuprous chloride, the preparation of which will be described in the special chapter on Absorbents.

The principal applications of the ordinary Orsat apparatus, with two or three absorbing pipettes, are: for controlling the efficiency of furnace fires by estimating the carbon dioxide in the chimney-gases; for estimating carbon dioxide, oxygen, and carbon monoxide in producer-gases, in gases from blast-furnaces, and from other sources.

F. Fischer (*Dingl. polyt. J.*, cclviii., p. 28) has employed the Orsat apparatus for estimating the acids and the oxygen in pyrites-kiln gases, for which purpose he charged the apparatus with petroleum in lieu of water, but this method is hardly used by practical men.

LUNGE'S MODIFICATION OF THE ORSAT APPARATUS.

This modification (described in *Chem. Ind.*, 1882, p. 77; *Dingl. polyt. J.*, ccxlv. p. 512), in addition to all the essential parts of an ordinary Orsat apparatus, contains a contrivance for burning *hydrogen* (and other gases) by means of heated palladium asbestos or palladium wire.

It is shown in Fig. 43. *a* is the gas-burette, *b*, *c*, and *d* are the usual U-tubes for absorbing carbon dioxide, oxygen, and carbon monoxide; *k* is the ordinary three-way cock; *e* is an additional glass tap, to which is fused a capillary tube, bent twice at a right angle. This is tightly joined by stout india-rubber tubing to the combustion-capillary tube *f*, which contains a thread of palladium asbestos, the preparation of which will be described later on, and which can be heated by means of the small spirit-lamp *g*, fixed in a spring clamp which, by means of the pivot-wire *i*, turns in a socket fastened to the wooden case, containing the apparatus. The U-tube *h* is exactly similar to the tubes *b*, *c*, and *d*, and is filled with water up to its capillary neck. The dotted U-tube shown at the left is filled with cotton-wool, and serves for retaining any tarry matters, soot, etc.

The apparatus is manipulated as follows:—First carbon

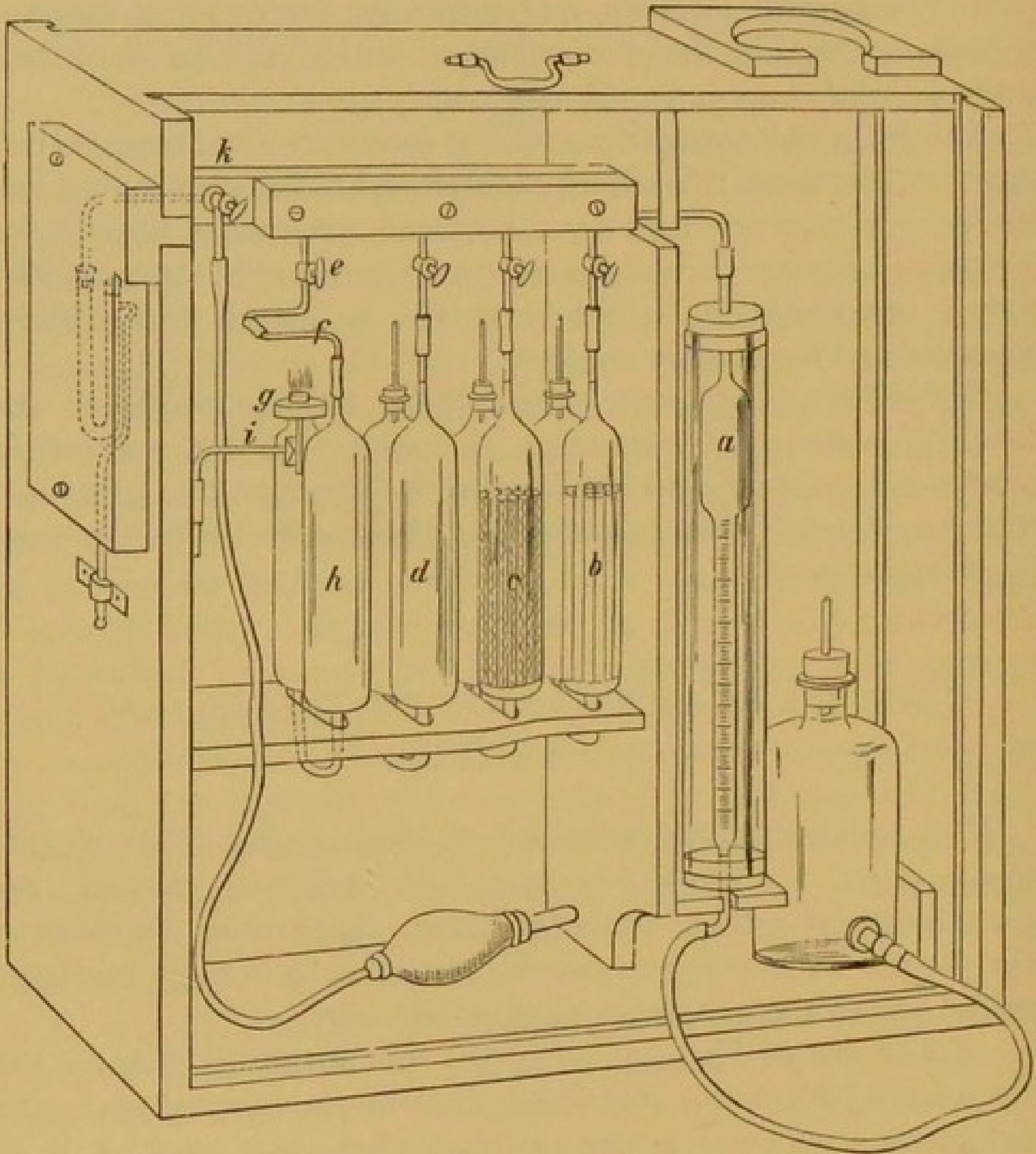


FIG. 43.

dioxide, oxygen, and carbon monoxide are absorbed in the usual manner, described *suprà*, p. 64. (If, however, there is but little carbon monoxide present, say not exceeding 2 or 3 per cent., it is preferable to omit the treatment of the gas with cuprous chloride solution, and to burn the carbon monoxide, the percentage of which is found by a special experiment, together with the hydrogen. Any ethylene present would be absorbed by the cuprous chloride together with the carbon monoxide.) Now air is admitted through the three-way cock *k*, and lowering the level-bottle connected with *a* to the gaseous residue contained in *a*, until the water goes down nearly to the zero mark in *a*, so that the total volume of gas in *a* is nearly 100 c.c. The air thus introduced will allow of burning a quantity of hydrogen corresponding to two-fifths of its volume (*i.e.*, twice the volume of oxygen contained in the air). This is sufficient for ordinary producer-gas ("Siemens gas"); but when analysing water-gas or similar mixtures containing a considerable quantity of hydrogen, one of the following modes of proceeding must be adopted. Either less than 100 c.c. of the gas must be employed for analysis; or if employing 100 c.c. of gas after the first combustion has taken place, and the contraction of volume has been noted, another quantity of air is introduced and the combustion is repeated; or, thirdly, oxygen in lieu of air is introduced through *k*, which necessitates only one combustion.

After reading off the volume of gas contained in *a* and the volume after admission of air (or oxygen), the spirit-lamp *g* is lighted and the capillary *f* is very gently heated; then the level-bottle is raised, tap *e* is opened, and the gas is passed from *a* through the capillary *f* into the pipette *h* and back again into *a*. During this operation one end of the palladium-asbestos thread, that opposite to the current of gas, should become red-hot. The volume of gas in *a* is measured, and the passage of the gas through *f* is repeated. If (which is usually not the case) a further contraction is now observed, the passage of the gas through *f* must be repeated once more. The residual gas is now finally measured, and two-thirds of the diminution of volume calculated as hydrogen.

In the case of a very high percentage of hydrogen, *e.g.* in water-gas, the oxygen of the air introduced will not suffice for burning all the hydrogen. In such cases it is preferable, as stated above, to employ oxygen for the combustion. If this has not been done, the fact of the volume of the residual gas in *a* remaining constant after passing it twice through *f* is not caused by the complete removal of hydrogen, but by that of oxygen. To make sure of this, a fresh quantity of air is mixed with the residual gas, and it is observed whether a further contraction takes place after passing the mixture through *f*.

The principal application of this apparatus is the estimation of free hydrogen along with carbon dioxide, oxygen, and carbon monoxide in producer-gas, water-gas, and similar mixtures. It is much more portable than Hempel's burette with its appendages, and the tests can be made in any locality and very quickly. Ethylene and other heavy hydrocarbons would be absorbed by the cuprous chloride, together with carbon monoxide; but they occur in such gases in quantities so small that they may be safely neglected, or rather calculated as carbon monoxide. If, however, they are to be accounted for, a second test should be made, leaving out the operation with cuprous chloride; this time the gas, after carbon dioxide and oxygen have been observed in the usual way, is at once mixed with an excess of air and burnt by the palladium-asbestos. By measuring the contraction produced, then absorbing the CO_2 by the receiver *b* filled with caustic-potash solution, and measuring the new diminution of volume, we obtain another estimation of the combustible gases (carbon monoxide, hydrogen, and ethylene) in the following way:—If the first contraction is diminished by one-half of the second contraction (that is that which takes place by absorption of the CO_2 formed in the combustion process), two-thirds of the difference represent the hydrogen; the carbon monoxide corresponds to the second contraction, according to the following formulæ:—

$2x$ vols $CO + x$ vols O yield $2x$ vols CO_2.
$2y$ vols $H + y$ vols O yield (condensed) H_2O.

Hence:—

First contraction (A) = $3y + x$.
Second ,, (B) = $2x$.

It follows from this that the carbon monoxide in the gas analysed is = B, and the hydrogen = $2\frac{A - \frac{B}{2}}{3}$.

If the numbers thus obtained agree closely with those found by the first test made in the ordinary way as described *suprà*, p. 72, we may conclude that no heavy hydrocarbons were present; indeed we must expect to find rather less CO_2 than demanded by theory, as part of it will be absorbed by the water contained in the apparatus (in order to diminish this error, the analysis should be performed as rapidly as possible). If, therefore, the CO_2 is in excess of that required on the assumption that only CO and H were present, we must conclude that heavy hydrocarbons were present. Equations might be given for calculating these, but their estimation in this way would not be very correct, so that we prefer leaving it aside. Ethylene by itself may be previously absorbed by bromine water, as we shall see in a later chapter.

Any *methane* present in the original gas will not be touched by the previously described operations; it remains with the nitrogen in the last remaining gas. We shall see later on that methane can be burned by means of a strongly heated platinum capillary, and such a capillary may also be employed in the Orsat-Lunge apparatus, in the place of the palladium-asbestos capillary, if that apparatus is to be used for the analysis of water-gas or producer-gas, where heavy hydrocarbons need not be taken into account.

In the case of gases containing much carbon monoxide the absorption of this constituent by cuprous chloride is sometimes incomplete, and the carbon monoxide left unabsorbed is burned afterwards in the treatment just described, together with the hydrogen. If this is suspected the gas remaining in *a* must be passed into *b*, in order to take out the carbon dioxide formed in the combustion of carbon monoxide, and the residual gas is finally measured in *a*. The contraction produced by this last operation is = the volume of carbon monoxide left unabsorbed by cuprous chloride.

Suppose a producer-gas to have given the following readings:—

1.	After absorbing the carbon dioxide . .	a contraction of 3·2 c.c.
2.	„ „ oxygen . . .	no contraction
3.	„ „ carbon monoxide . .	a contraction of 24·2 c.c.
4.	After mixing with air for combustion . . (That is, adding 24·2 − 0·9 = 23·3 c.c. air)	„ 0·9 „
5.	After burning the mixture by the palladium .	„ 10·8 „
6.	„ absorbing the CO_2 formed from the CO, unabsorbed in No. 3, by the process No. 4	„ 11·4 „

That means that in No. 3, 24·2 − 3·2 = 21·0 per cent. carbon monoxide had been absorbed; from No. 6 it follows that 11·4 − 10·8 = 0·6 must be added to this, bringing up the total percentage of carbon monoxide to 21·6 per cent. The contraction of volume after burning the residual gas and deducting the CO present in this (the volume of CO_2 formed is exactly equal to that of the CO burned) is 10·5, two-thirds of which = 7 per cent., less the 0·6 per cent. carbon monoxide unabsorbed = 6·4, is the original percentage of hydrogen. Hence the composition of the original gas is—

Carbon dioxide . . .	3·2 per cent.
Oxygen	none
Carbon monoxide . .	21·6 per cent.
Hydrogen . . .	6·4 ,,
Nitrogen (with a little methane)	68·8 ,,
	100·0 per cent.

FURTHER MODIFICATIONS OF THE ORSAT APPARATUS.

The chemical literature contains a great many descriptions of various forms of apparatus of this class, both for the rapid examination of producer- or smoke-gases, and for the analysis of more complicated gaseous mixtures. Many of these are not obtainable in commerce. We here enumerate briefly the more important apparatus of this class.

Gebhardt's gas-analyser (*Chem. Zeit.*, 1907, p. 283, sold by A. Primavesi, Magdeburg) serves for estimating the excess of oxygen in fire-gases. It consists of a measuring burette, an absorbing vessel filled with phosphorus, and an absorbing bottle with india-rubber pumps.

Ströhlein & Co. at Düsseldorf (*Z. für chem. Apparatenkunde*, 1907, p. 323) describe an apparatus for estimating carbon dioxide in smoke-gases. The gas to be tested forces a certain quantity of caustic solution, through which it passes, into a measuring vessel, where the percentage of CO_2 can be directly read off.

The apparatus of Sodeau (*Chem. News*, 1904, lxxxix. p. 61; B. P. 12225 of 1906, sold by Brady & Martin, Newcastle-on-Tyne) is also especially applicable to the examination of himney-gases. Instead of the cuprous chloride pipette and he palladium-combustion tube it contains a combustion pparatus, consisting of two separate vessels, the bulb O and he aspirator CR, as shown in Fig. 44; or it may be shaped like Hempel pipette for solid absorbents, as shown *infrà*, Fig. 51, . 85, provided with a straight instead of with a bent capillary ube. The bulb O contains a platinum wire, 0·25 to 0·3 mm.

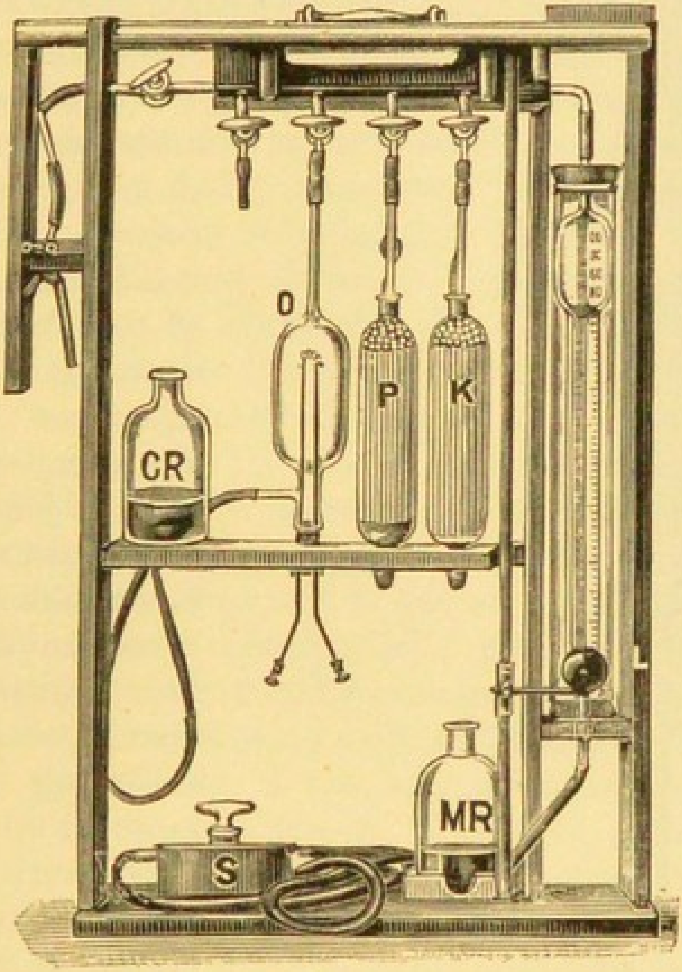


FIG. 44.

n diameter, attached to brass electrodes, and is heated by current of 5 ampères. The lens L affords increased accuracy n reading. Pipettes K and P serve for the determination of arbon dioxide and oxygen. CR is a movable reservoir for he rapid joint estimation of carbon monoxide and hydrogen a more detailed description is given in Lunge-Keane's *Technical Methods of Chemical Analysis*, vol. i., part 1, pp. 203 *et seq.*; n pp. 219 *et seq.* another apparatus of Sodeau is fully described).

The apparatus of Babb (*J. Amer. Chem. Soc.*, 1905, xxvii. . 156) comprises six absorbing pipettes, holding 250 c.c. each, an explosion tube, two dry batteries, an induction coil, and two level bottles. The absorbing pipettes are so constructed that the gas must traverse the absorbing liquid. Bement (*ibid.*, p. 1252) adds to this apparatus an india-rubber pump for squirting the absorbing liquid into the gas.

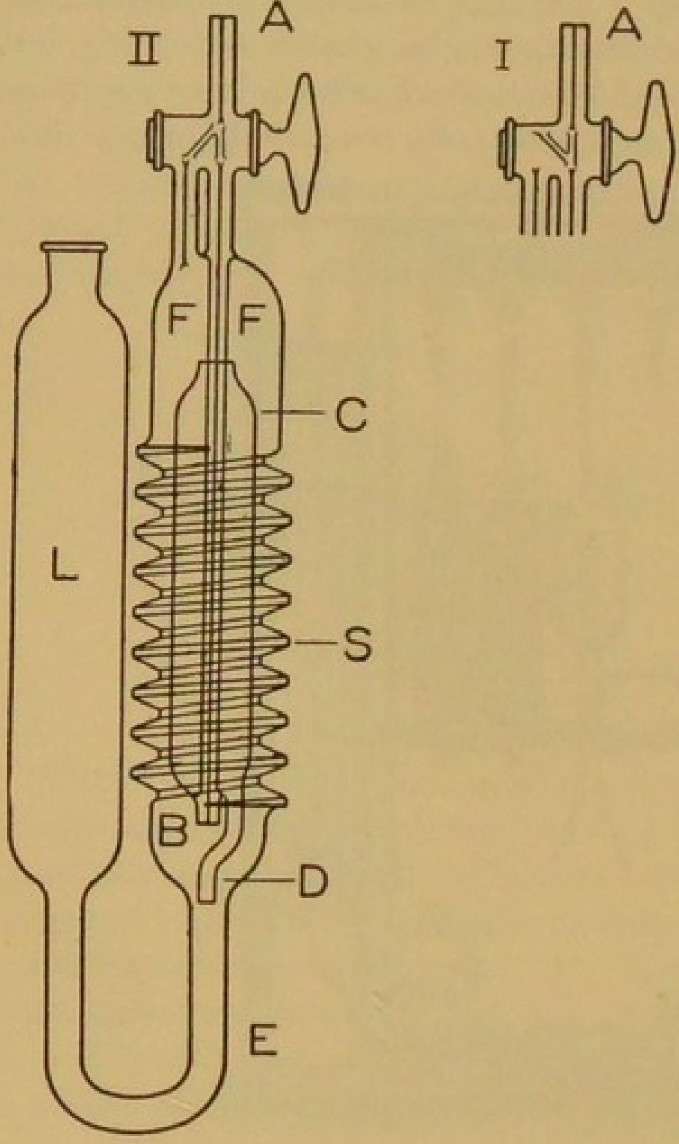


FIG. 45.

Barnhardt and Randall (*Z. für chem. Apparatenkunde*, 1908, p. 337) describe an Orsat apparatus in which the measuring-tube is closed at the top by a six-way cock, to the capillary tubes of which the absorbing pipettes are radially joined.

Siebert and Kühn, of Cassel, sell an apparatus made on the place of the Gasmotorenfabrik Deutz, containing four absorbing pipettes of special construction which turn on a brass plate, so as to be connected in rotation with the burette.

The apparatus of Wencélius (*Stahl u. Eisen*, 1902, p. 664; sold by Ströhlein & Co., of Düsseldorf) contains two burettes, holding 100 c.c. each, one of them for readings from 0 to 50, the other from 50 to 100 c.c., and absorbing pipettes for carbon dioxide and oxygen.

L. M. Dennis (*J. Ind. and Engin. Chem.*, Dec. 1912) describes an absorption bottle shown in Fig. 45. The gas mixture enters the pipette through the capillary A (the stop-cock being in position I), and passing downward through the capillary, escapes at B. It then rises, and in so doing follows the spiral S. The rising gas carries some of the absorbing iquid with it, and this liquid then flows down on the inside of the cylinder C and mixes with the main body of the absorbent again at D. After the gas has risen through the spiral and has collected in the space F, the stopcock is turned through 180° to position II, and the gas is then drawn back nto the burette.

The same author (*Gas-Analysis*, 1913, pp. 90 *et seq.*) describes the modifications of the Hempel apparatus, where it is intended or exact gas-analysis, with mercury as confining liquid.

Dennis points out several drawbacks connected with the use of the ordinary Orsat apparatus, such as the incorrect position of the measuring burette, etc. To avoid these, he has designed the modification shown in Fig. 46, which is manuactured by Greiner & Friedrichs, Stützerbach in Thüringen (Germany). The burette B has a capacity of somewhat more han 100 c.c., and is graduated from a point near the bottom upward to the stopcock J. This is a three-way stopcock, the position of which is shown by means of a black glass ⊣ fused o its outer surface. The capillary tube connecting J with the pipettes and with the stopcock K has an external diameter of mm. and an internal diameter of 1 mm. In fusing on the branch capillaries which extend downward to the three pipettes, he internal diameter of the capillary should, at no point, be much greater than 1 mm. if the apparatus is properly made. The three absorption pipettes, E, F, and G, are of the form already described, and are filled, respectively, with solutions f potassium hydroxide, alkaline pyrogallol, and ammoniacal uprous chloride. They are connected with the capillary tube rom the burette by means of pieces of soft, black rubber tubing f 1·5 mm. thickness of wall, and these rubber tubes are held in place by wire hooks that pass through the blocks behind the joints, and have threaded ends upon which small set screws are placed. This method of attachment renders it easily possible o remove all the glass parts from the frame. Into the open ends of the three level-tubes of the pipettes are inserted one-hole rubber stoppers, and through the openings of these stoppers pass the branch-tubes from the tube SS, that is 7 mm. external diameter and 1 mm. thickness of wall. This tube passes downward and is joined by a piece of rubber tubing to the upper side of the stopcock attached to the cylindrical vessel T, which in turn is connected with V by the glass tube shown by the dotted line. After the pipettes have been filled with the several reagents, the stoppers connecting the level-tubes with the tube SS are inserted in place, and the protecting reservoir VT is half filled with water. As the gas is driven over from the burette into the pipette and is drawn back into the burette, the water in VT rises and falls, but protects the reagents at all times from contact with the air. The level-bottle L is held in place by a clamp when the apparatus is in transport.

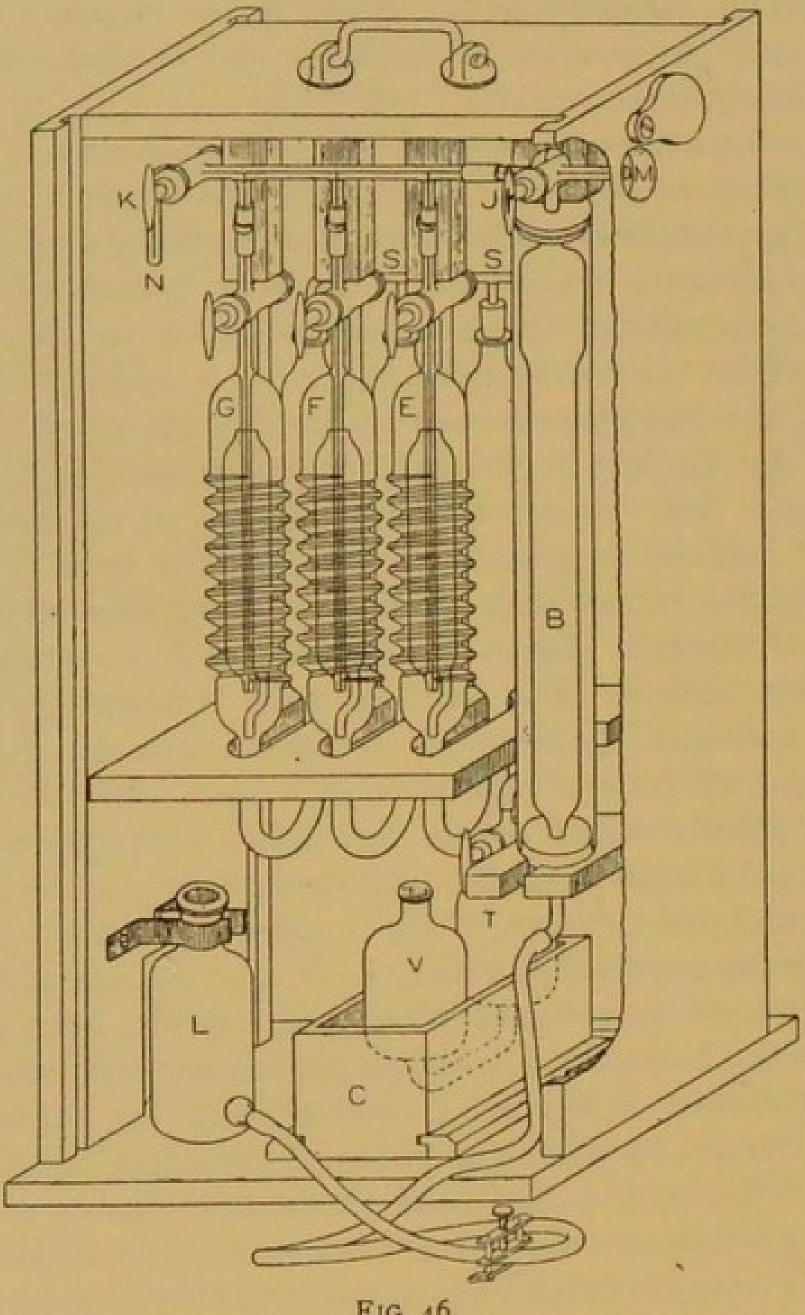


FIG. 46.

After the absorbable gases have been removed from the gas mixture, the combustible residue may be burned, if so desired, by connecting the capillary M, which has an external diameter of 6 mm. and a bore of 1 mm., with a combustion pipette or other suitable device. The case containing the apparatus is 57 cm. high, 27 cm. wide, and 16 cm. deep. The panels forming the front and back of the case are removed when the apparatus is in use. As illustrative of the speed, accuracy, and uniformity of the results yielded by this apparatus, the following analyses of a mixture of carbon dioxide, oxygen, and carbon monoxide may be cited. A single passage of the gas mixture in one minute into the first absorption pipette serves to completely remove the carbon dioxide. In the determination of oxygen and carbon monoxide each gas was twice passed into the absorption pipette, the first time in two minutes, the second time in one minute.

	I.	II.	III.	IV.
	Per cent.	Per cent.	Per cent.	Per cent.
Carbon dioxide	3·1	3·1	3·2	3·1
Oxygen	6·0	6·0	5·9	5·9
Carbon monoxide	22·5	22·6	22·6	22·7

Further modifications of the Orsat apparatus have been described by:

Thörner (*Chem. Zeit.*, 1891, p. 768).

Hankus (*Oesterr. Z. f. Berg u. Hüttenwesen*, 1899, p. 81; *Stahl u. Eisen*, 1903, p. 261).

Fieber (*Chem. Zeit.*, 1905, p. 80).

Neumann (*ibid.*, 1905, p. 1128).

Wilhelmi (*Z. angew. Chem.*, 1911, p. 870).

Lomschakow (sold by Ludwig Mohren, of Aix-la-Chapelle).

Preuss (*Z. angew. Chem.*, 1912, p. 2112).

Bendemann (*J. Gasbeleucht.*, 1906, p. 853).

Rowicki (*Oesterr. Z. f. Berg u. Hüttenwesen*, 1905, p. 537).

Heinz (*J. Gasbeleucht.*, 1905, p. 367).

Hahn (*Z. Verein. deutsch. Ingen.*, 1906, p. 212; 1911, p. 472; 1913, p. 954; *J. f. Gasbeleucht.*, 1906, pp. 367 and 474; 1911, p. 472).

HEMPEL'S APPARATUS.

These apparatus (described by Hempel in his treatise *Ueber technische Gasanalyse*, 1877, and *Gasanalytische Methoden*, 4th ed., 1900, p. 29) have proved most useful and have acquired a large radius of application. Hempel started by modifying the "gas-pipettes," previously described by Ettling and Doyère for the separate absorption and estimation of the single constituents of a gaseous mixture, which are attached to a gas-burette by means of a connecting capillary. This secures the advantage that the measuring of the gas and its treatment with the various absorbents can be separately performed at leisure and in a very efficient way, with a high degree of accuracy, and employing water as a confining liquid.

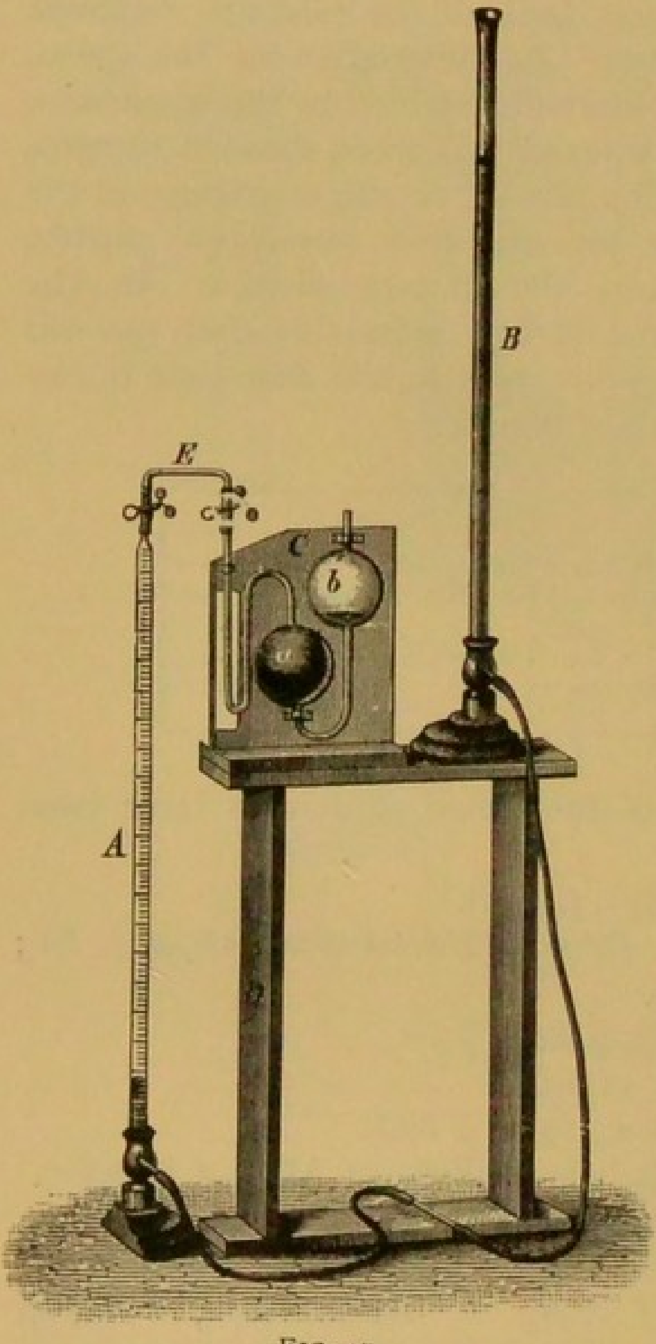


FIG. 47.

The ordinary Hempel's gas-burette is shown in Fig. 47, in connection with an absorbing-pipette. It consists of two cylindrical glass tubes, A and B, 1·5 cm. wide and 55 to 68 cm. long, whose bottom ends are contracted and turned in a right angle. These tubes are cemented into stands made of thin cast-iron or of polished black wood, their contracted ends passing out sideways at a right angle. The bottom outlets have an outside diameter of 4 mm.; they are thickened at the outer end, so that they can be easily and tightly connected with an india-rubber tube, about 120 cm. long, which is preferably interrupted in the middle by a piece of glass tubing, and which allows of placing the tubes at a higher or lower level. The measuring-tube A at the top ends in a thick capillary, 0·5 to 1 mm. wide, and 3 cm. long, upon which a piece of thick india-rubber tubing, 2 mm. bore, 6 mm. outside diameter, and 5 cm. long, is drawn and fixed gas-tight by means of a silk-covered copper wire. Closely above the capillary the elastic tube is closed by a small pinchcock, which is taken off when not required for use. From this top end down to the bottom mark, 3 or 4 cm. above the foot, tube A holds 100 c.c., divided into fifths of a cubic centimetre, and showing on one side the figures from 0 to 100, on the other from 100 to 0. The level-tube B is a plain glass tube, open at the top.

In lieu of this, burettes with a water-jacket may be used, as shown in Fig. 48. This jacket, 3 cm. wide, serves for keeping the temperature of the gas constant; it is provided at top and bottom with side-branches through which, if needed, water may be run in a constant stream. The burette is fixed in this water-jacket by means of india-rubber corks. In most cases these jackets, which make the apparatus less handy, are not required.

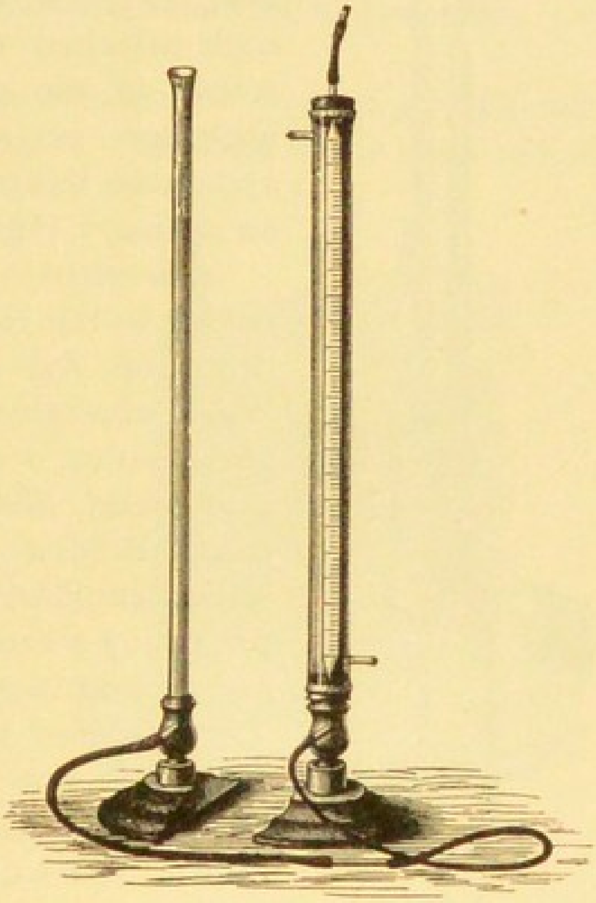


Fig. 48.

For the analysis of gaseous mixtures which cannot be confined over water, because some of their constituents are too easily absorbed by it, Hempel employs what is called the *modified Winkler's gas-burette*, Fig. 49. This is at the bottom closed by a three-way glass tap *c*, and at the top by a simple glass tap *d* or by a pinchcock; the space between these taps contains 100 c.c., divided into fifths. Before introducing the gas, the measuring-tube *b* must be completely dried, *e.g.*, by rinsing it first with alcohol, then with ether, and then blowing a rapid current of air through it. It is charged with the gas by passing this through it until all the air has been expelled, for which purpose the pinchcock attached to *c* is connected with the source of the gas, and the tap *d* with an aspirator, or *vice versâ*. Otherwise this apparatus is arranged and manipulated like an ordinary Hempel burette.

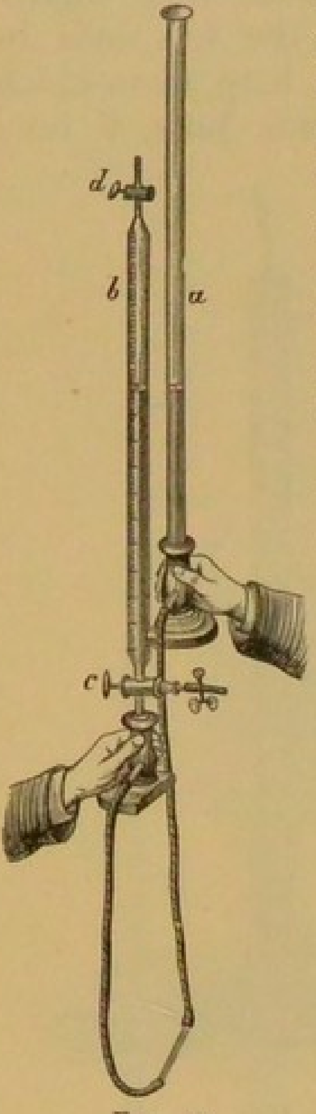


FIG. 49.

Absorption-pipettes.—Various such pipettes belong to the Hempel apparatus. In Fig. 47 (*suprà*, p. 82) is shown what is called the *simple absorption-pipette*. It consists of two glass bulbs, *a* and *b*, fixed on a wooden or iron stand, and communicating by a bent tube. Bulb *a* is connected with the thick-walled capillary U-tube, 0·5 to 1 mm. bore, projecting a centimetre or two over the stand and ending in a piece of india-rubber tubing. This is closed by a short glass rod when the pipette is not in use, and by a pinchcock when this is the case. Bulb *a* holds 150 c.c., bulb *b* 100 c.c., so that when *a* is charged with 100 c.c. of gas, there is still room for the absorbing liquid. Behind the capillary U-tube a white porcelain slab is fixed for the purpose of making the liquid thread more easily visible. The india-rubber tubes must be of the best quality, and must be fastened on by thin wire in order to prevent leakages and other trouble. The absorbing liquid is poured into the wide tube attached to *b*, carefully sucking out the air from *a* through the capillary tube. This is done until the liquid has completely filled bulb *a* and has entered into the capillary; bulb *a* must be nearly empty.

As stated above, the capillary U-tube of *a* is during use closed by an elastic tube and pinchcock. When it is to be put out of use, the piece of glass rod is put into the outside end of the elastic tube, while the pinchcock is closed, and this cock is only removed subsequently ; otherwise on putting in the glass rod, air would be forced in and the thin column of liquid in the U-tube may be broken. Should this happen anyhow, the capillary tube is emptied by sucking for a moment at *a*, and filled again by blowing air in the opposite direction. The end of the tube coming out of bulb *b*, when the pipette is not in use, is closed by a cork, which must be removed before using the pipette.

Fig. 50 shows the pipette employed when using *fuming oil of vitriol* as an absorbing liquid. Here bulb *a* is surmounted by a smaller bulb, *d*, filled with small bits of glass, which enlarges the absorbing surface and renders agitation unnecessary. The ends of this pipette are closed by small glass caps, which may be made quite tight by means of small india-rubber rings.

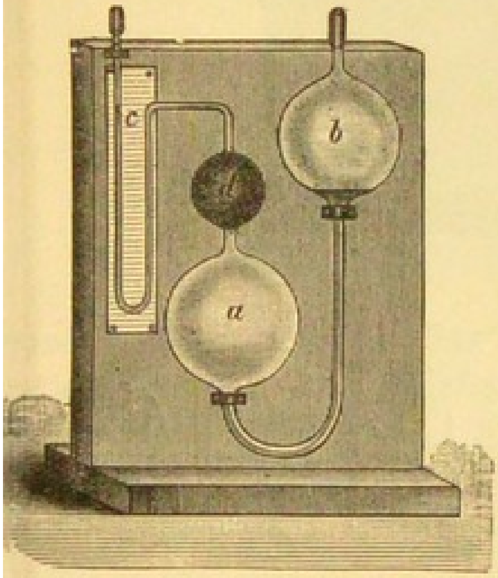


FIG. 50.

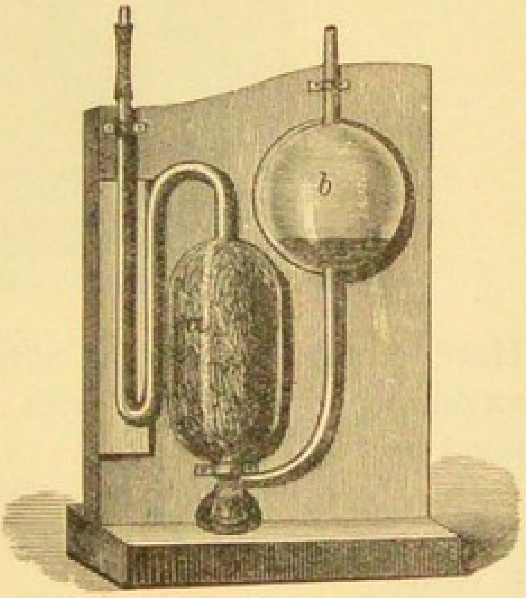


FIG. 51.

A pipette for the use of *solid reagents*, *the* "*tubulated absorption-pipette*," is shown in Fig. 51. Here, instead of a bulb there is a cylindrical part *a*, with a neck at the bottom. Through this the solid reagent—*e.g.* sticks of phosphorus—is put in together with water, whereupon the neck is closed by a soft india-rubber stopper, and the pipette is placed in the proper position. The tube over bulb *e* may be connected with another pair of bulbs, as shown in Fig. 52, where this is necessary.

The *composite absorption pipette*, Fig. 52, is used for absorbents which suffer change in contact with atmospheric air, such as the alkaline solution of pyrogallol, or the hydrochloric or ammoniacal acid solution of cuprous chloride; also for such as give off irritating vapours, like bromine water.

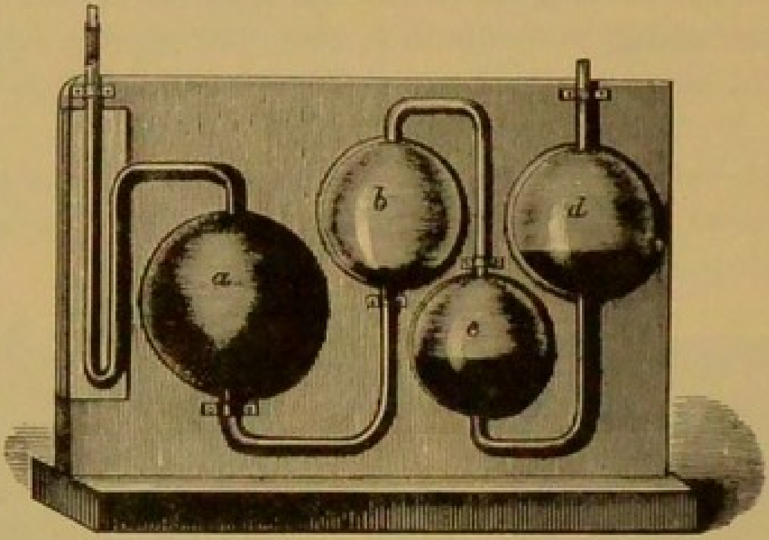


FIG. 52.

Here a second pair of bulbs, *c* and *d*, form a water lute, excluding the contact with the outside air. These pipettes must be filled through the capillary U-tube in connection with bulb *a*, by connecting its india-rubber end with a funnel-tube of about a metre in length, through which the absorbing liquid is poured.

Fig. 53 shows an improvement in this pipette, consisting in a short branch attached to the lowest point of the connecting tube between *a* and *b*, closed by a pinchcock or glass rod, for the purpose of charging the pipette. After doing so, the pinchcock is replaced by a glass rod. The stand is cut out accordingly.

General Arrangement of Hempel's Apparatus.—The general arrangement is shown in Fig. 47 (*suprà*, p. 82). The burette A and the capillary of pipette C, after putting on pinchcocks as shown in the drawing, are connected by the glass capillary E, made of a tube 18 cm. long, 6 mm. outside diameter, and 1 mm. bore, by bending it on each side into a right angle, with limbs 4 or 4½ cm. long, the ends of which are rounded off. The pipette is placed on a wooden bench, about 46 cm. high, 37 cm. long, and 10 cm. broad.

A. C. Cumming (*J. Soc. Chem. Ind.*, 1913, p. 9) describes a modification of the Hempel double pipette, which he provides with a special tube for filling with the reagent. A portable Hempel apparatus has been devised by L. M. Dennis (*Gas-Analysis*, 1913, p. 69).

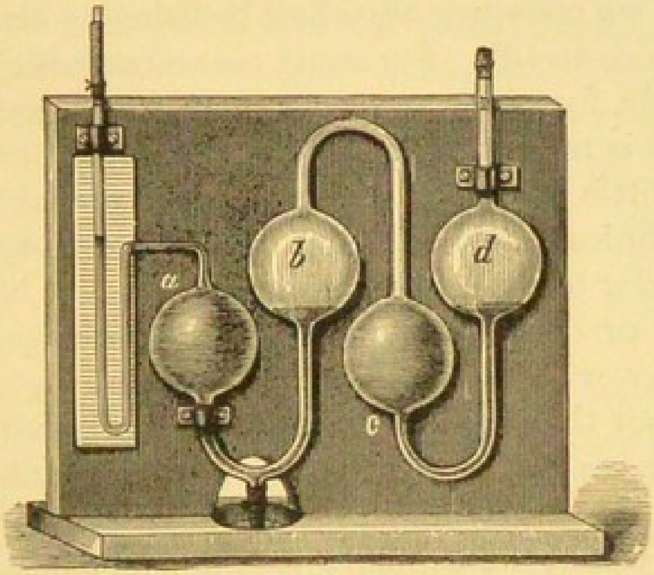


FIG. 53.

The remark made in the case of the gas-volumeter (*suprà*, p. 27), according to which the apparatus should be placed in a room of nearly constant temperature, since a fluctuation of merely 1° C. causes an analytical error of 0·3 per cent., applies equally to Hempel's (like most other) ordinary apparatus for gas-analysis, but this is avoided by the water-jacketed burette, shown *suprà*, Fig. 48.

Manipulation of the Hempel Apparatus.—Remove the connecting capillary tube E (Fig. 47), lift up the level-tube B (previously filled with water) with one hand, and with the other hand open the pinchcock of the burette A till this is full and the water begins to run out. Now connect the india-rubber tube of the pinchcock with the aspirating-tube, already filled with the gas, place the level-tube B on the floor of the room, and open the tap again, whereupon the water flows back into the level-tube and the gas is drawn into the burette. Allow a little more than 100 c.c. gas to enter into A, compress this by raising B, until the water has risen in A above the zero mark, compress the connecting elastic tube with the fingers close to the joint, place B again lower, and by cautiously loosening the elastic tube, allow the water to run out until the zero mark has just been reached. Then the connecting tube being still compressed, open the pinchcock of burette A for a moment, whereupon the gas contained in A gives up its surplus pressure and assumes that of the atmosphere. The burette now contains exactly 100 c.c., of which we convince ourselves by bringing the water to the same level in A and B. For exact measurements it is necessary to wait a little for the water to run down completely, and in such cases it is more convenient not to employ exactly 100 c.c. gas, but a little more or less as the case may be; but for ordinary technical estimations it is preferable to employ just 100 c.c. in order to save calculations.

We now proceed to connect the absorbing-pipettes, one after the other, with the burette, as shown in Fig. 47. For this purpose we put the capillary E, already connected with pipette C, on the burette A. In order to avoid any bubbles of air to be enclosed, the india-rubber tube above the pinchcock of A is filled with water, the capillary E is put in, whereby it is completely filled with liquid, and now the other end of E is put into the india-rubber tube of pipette C, which is at the same time emptied of air by compressing it between two fingers. If now the pinchcock on A is opened, and the level-tube B is raised at the same time, the gas is forced from A through E into the bulb *a* of pipette C, driving its liquid contents into bulb *b*. When this has taken place, we drive about 0·5 c.c. of water from A through E, whereby this capillary is rinsed out and freed from any absorbing liquid it may have retained. The gas is now enclosed between two liquids, viz., the absorbing liquid in the pipette C, and the water contained in the capillary E. Now close both pinchcocks, take the pipette C off, and bring about the absorption of the gas contained in bulb *a*, by gently (not violently) shaking the pipette. The absorption of the gas by the liquid in C is generally finished in about two minutes, sometimes even more rapidly, *e.g.* in the case of carbon dioxide. Now connect C again with capillary E, place the level-tube B on the floor, and, by cautiously opening both pinchcocks, cause the unabsorbed gas to re-enter the burette A, taking care that the absorbing liquid at the end just gets into the end limb of the capillary belonging to C, but not into the connecting capillary E. In the case of liquids inclined to frothing, such as the alkaline solution of pyrogallol, this cannot be always avoided; if, in consequence of this, the india-rubber joints should become so slippery that the capillary tube will not hold fast, but slides off, the joints must be washed with water (the pinchcocks being closed), and their ends moistened with a little dilute acetic acid introduced into the end of the elastic tube.

Now the pinchcocks are closed, capillary E is taken off, the open ends of the elastic tubes are closed by their glass rods, the level-tube B is cautiously raised up to the point where both levels coincide (as shown in Fig. 49, p. 84), and, after waiting a couple of minutes for the water to run down, the reading is taken, placing the liquid level in the same plane as he eye of the manipulator.

In the same way, by employing different pipettes, a second, third, and further constituent of the gaseous mixture can be absorbed and estimated.

The principal applications of the Hempel apparatus are he following:—

(*a*) Estimation of *carbon dioxide* in mixtures with air, in chimney-gases, gases from blast-furnaces, lime-kilns, gas-producers, etc., by means of a simple absorption-pipette, Fig. 47, filled with a solution of caustic potash.

(*b*) Estimation of *oxygen* in atmospheric air, chimney-gases, producer-gases, etc. This takes place after removing he carbon dioxide as mentioned *sub a*, either by means of a oncentrated alkaline solution of pyrogallol, employed in a omposite absorption-pipette, Fig. 52, or by means of a ubulated absorption-pipette, Fig. 51, filled with small rolls of opper wire gauze, immersed in liquor ammoniæ; or else as well in the presence of carbon dioxide, by such a pipette filled with thin sticks of phosphorus under water.

(*c*) Estimation of *carbon monoxide* in producer-gas, blast-urnace gas, chimney-gases, etc. After absorbing carbon ioxide and oxygen, the carbon monoxide is absorbed by an mmoniacal or hydrochloric acid solution of cuprous chloride, which must be employed in a composite absorption pipette, Fig. 52, *suprà*, p. 86.

(*d*) Estimation of *hydrogen* by combustion with oxygen, either over palladium-asbestos or by explosion. The former method is carried out by replacing the connecting capillary tube E, Fig. 47, by a similar tube containing a thread of asbestos fibre, coated with metallic palladium, as will be described in a following chapter, and heated as described *suprà*, p. 75, in connection with the Lunge-Orsat apparatus.

(*e*) Estimation of *methane*. This is always performed by combustion with oxygen, either by explosion or by a heated platinum wire; in the presence of hydrogen this gas must be first removed by palladium sponge, as mentioned *sub d*, and described in a later chapter. For the determination of methane, Hempel has constructed a special "*explosion-pipette*." The earlier form of this, even now the more usual form for technical gas-analysis, is shown in Fig. 54; it is an ordinary simple pipette, provided with platinum electrodes at *k* and a large greased stopcock at *d*, and filled with water or dilute solution of potassium hydroxide. An improved form of pipette, in which mercury is used as confining liquid, is shown in Fig. 55; here the second bulb of the pipette is replaced by a level-bulb *a*, attached by a piece of stout india-rubber tubing. It is advantageous to have a small stopcock fitted to the top of the capillary tube at *c*, so that the mixture of gas and air or oxygen can be fired without risk of loss by leakage. (The whole

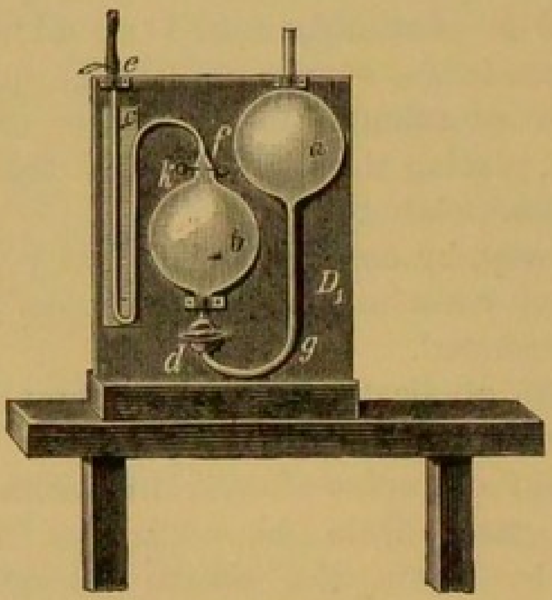


FIG. 54.

arrangement of Hempel's apparatus will be described later on, in the chapter on the Combustion of Gases.)

To carry out the determination of methane, the gas remaining after removing the constituents enumerated *sub a*, *b*, *c*, *d*, is syphoned over into the explosion pipette, the necessary quantity of air or oxygen added in the same manner as when burning hydrogen over palladium asbestos, the total volume measured and passed over into the pipette, where it is mixed by gentle shaking; the water in the burette is syphoned over, until the capillary tube of the burette is filled, when the tap at *c* (Figs.

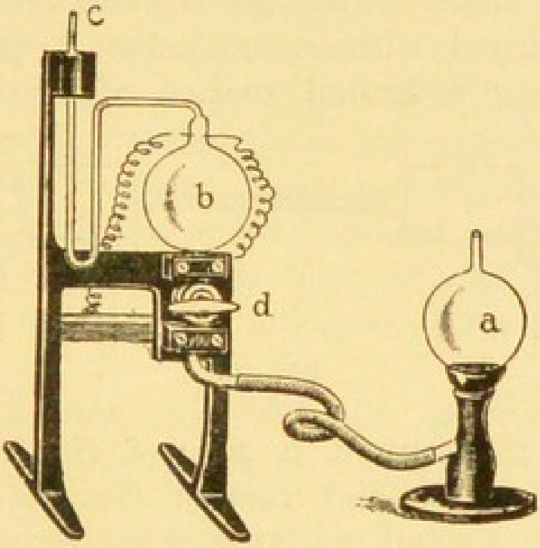


FIG. 55.

54 or 55) is closed. The pressure on the mixture is slightly educed before the explosion, by lowering the pressure bulb *a*; ap *d* is then closed, and the gases are exploded by attaching he terminals of a small Ruhmkorff coil to the electrodes of the pipette. After the combustion, the gas is syphoned back into he burette, and the carbon dioxide formed is determined by bsorption with caustic potash.

The quantity of air or oxygen to be added for the combustion must be calculated as follows. The ratio of combustible o incombustible gases must be no less than 26 and no more han 64 to 100, in order to be sure that no nitrogen is imultaneously oxidised (*Bunsen*, *Gasometrische Methoden*, 2nd d., p. 72). A good working proportion is 50 : 100, bearing n mind that the oxygen required theoretically for the ombustion of the methane, according to the equation:

$$CH_4 + 2O_2 = CO_2 + 2H_2O,$$

is included in the combustible gases, the excess forming part of the incombustible gases. The choice between air and oxygen will accordingly be decided by the volume of the gas to be dealt with and its content of methane. Oxygen from the ordinary commercial oxygen cylinders can be conveniently used, the percentage of real oxygen in it having been previously determined, One-third of the total contraction, after the absorption of carbon dioxide, represents the volume of methane present in the original gas mixture.

Preferable to this somewhat risky explosion process is the *combustion of methane by a heated platinum wire.* Methane is completely burned, without explosion, by passing it, mixed with oxygen, over a heated surface of platinum. Winkler (*Z. anal. Chem.*, 1889, xxviii. p. 269; *J. Soc. Chem. Ind.*, 1889, p. 570) designed a modified form of Hempel pipette for this purpose, in which a small platinum spiral, enclosed in the bulb of the pipette, is heated by an electric current. A much more convenient device for this method of determination is the Drehschmidt capillary tube (*Ber.*, 1888, p. 3245) shown in Fig. 56. It consists of a seamless platinum tube, 20 cm. long, 2 mm. thick, and 0·7 mm. internal diameter, containing three or four pieces of platinum wire. Pieces of brass tubing are soldered to the ends of the platinum tube, to form connections with the burette and the pipette. Two small cooling cylinders (through which water is made to flow), also made of brass, are fixed on to the brass tubes, just above the bend. The tube must be tested before use to make sure that it is air-tight. For this purpose the tube is made red-hot, closed at one end, and through the other end air is forced in at a pressure of about 0·3 m. mercury. If the tube is then placed under water, any leakages are indicated by bubbles of air appearing on the water. To carry out the combustion, this capillary tube is attached by rubber connections to the burette and to a pipette

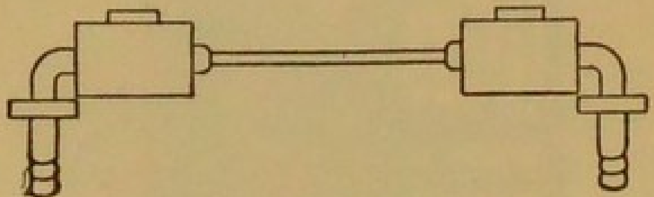


FIG. 56.

arged with caustic potash solution in the usual way, and e mixture of gas (or air) is obtained, as described above. he capillary is then heated to a bright red heat, preferably y a flat-flamed Bunsen burner, and the gaseous mixture is assed twice backwards and forwards over the heated platinum. he reading is taken after a final absorption in the potash ipette; one-third of the total contraction represents the ethane present.

Formation of Oxides of Nitrogen in Combustion Pipettes.— . H. White (*J. Amer. Chem. Soc.*, 1901, p. 476) stated that oxides f nitrogen are formed when hydrogen is burned with oxygen nd air by electrically heated platinum; but Rhodes (as quoted y Dennis in *Gas-Analysis*, p. 153) found that this is not the se to a measurable extent, where the conditions laid down y Dennis and Hopkins (*ibid.*, 1899, p. 388) are observed, and at is: that the platinum spiral is heated only to dull redness uring the combustion, and is kept at dull redness for no nger than sixty seconds after the gases have been introduced to the pipette.

Several *modifications of Hempel's apparatus* have been escribed by other chemists, of which we mention the llowing:—

Babbitt in *J. Amer. Chem. Soc.*, 1904, xxvi. p. 1026, describes "stationary" Hempel apparatus devised by W. J. Knox, in hich the pipettes are suspended on a horizontal rod, while e burette and level-tube are fastened to a vertical rod in ch a manner as to permit free lateral motion.

De Voldere (*Z. für chem. Apparatenkunde*, 1907, ii. p. 344) stead of the level-tube *b* of the Hempel apparatus employs level-bottle with a lateral tube, and instead of the burette *a* uses a Pfeiffer's burette (*Z. angew. Chem.*, 1907, p. 22), as will described later on.

Hill (*Proc. Chem. Soc.*, 1908, xxiv. p. 95) attaches a three-ay tap to the downward branch of the connecting capillary. o does Gawalowski (*Z. anal. Chem.*, 1911, p. 435).

Spencer (*Berl. Ber.*, 1909, p. 1786) recommends a special p for the connecting-tube between the burette and the bsorbing-pipettes, in order to fill this tube with liquid.

Knowles (B. P. 27545 of 1910) places the absorption-pparatus on a hinged support, so that on turning this support

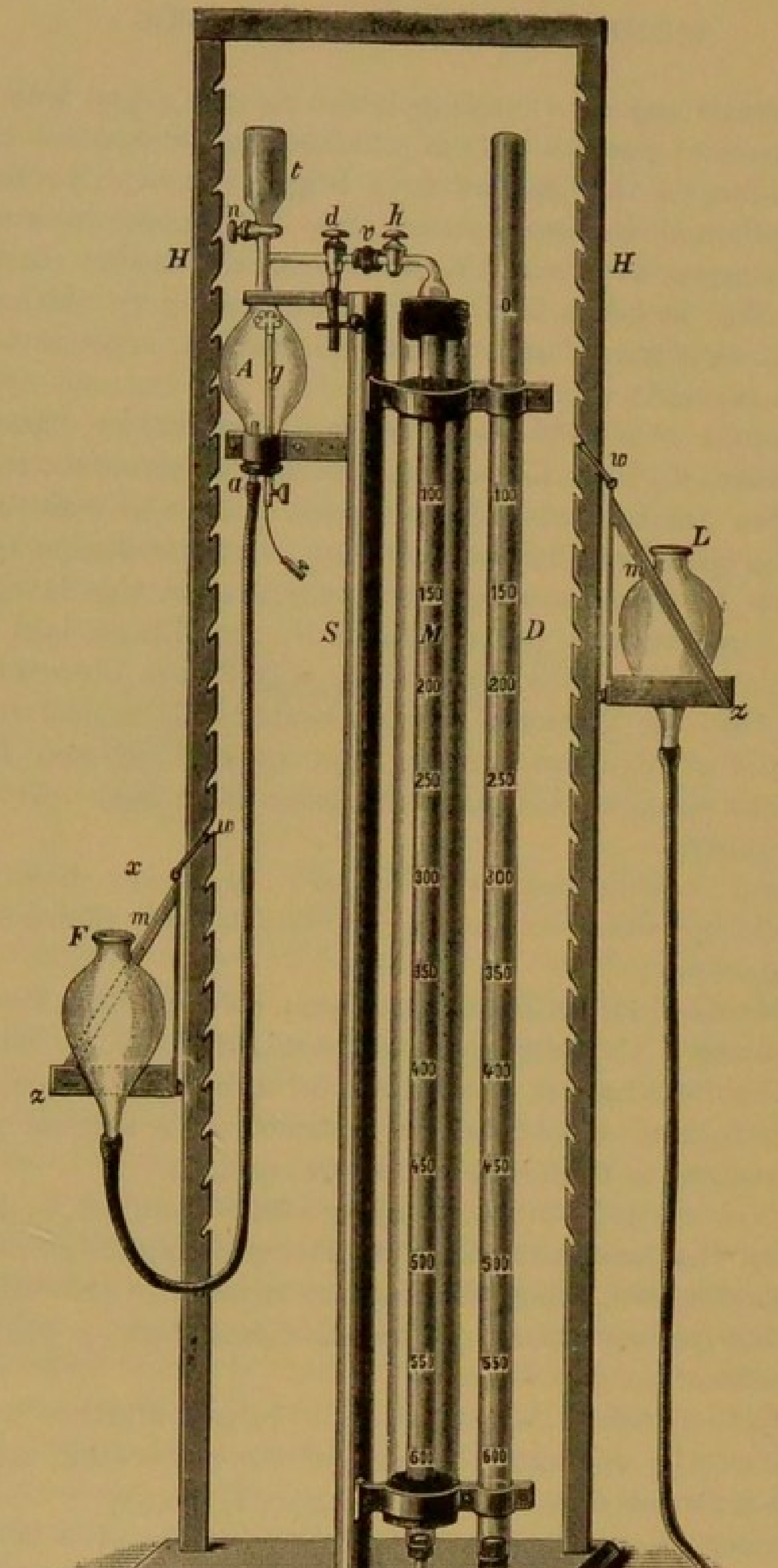

t
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FIG. 57.

nto a specified position, the beaker containing the absorbent iquid may be removed and recharged.

Göckel (*J. Gasbeleucht.*, 1911, p. 228) places in Hempel's omposite pipette (p. 86) the branch tube, intended for filling, t the top.

Hüfner (Ger. P. 244335; *Z. angew. Chem.*, 1912, p. 1665) escribes an apparatus by which the gas is always measured nder atmospheric pressure.

Anderson (*Z. angew. Chem.*, 1914, i. p. 23) provides the nlet-capillary with a 3 mm. bulb, to retain any absorbing quid squirting over.

FERDINAND FISCHER'S APPARATUS.

This apparatus (*Z. angew. Chem.*, 1890, p. 591) has been pecially designed for the analysis of producer-gas, water-gas, nd similar mixtures. It is a simpler form of apparatus than hose formerly described by Frankland and Ward (*J. Chem. Soc.*, 853, vi. p. 197), and later on modified by M'Leod (*ibid.*, 1869, xii. p. 313) and Thomas (*ibid.*, 1879, xxxv. p. 213). It is sually worked with mercury as confining liquid.

Fig. 57 shows this apparatus. Its essential parts are the ulb or laboratory vessel A, in which the absorptions and ombustions are effected, the water-jacketed measuring-tube M nd the levelling-tube D. The upper part of A must be ufficiently wide to prevent the adherence of drops of liquid. The measuring-tube M is either graduated in cubic centimetres r in millimetres. In the latter case, which is represented in he drawing, the tube must be calibrated by mercury in the rdinary manner. Pressure bulbs, F and L, supported on ooden blocks *z*, and movable in the notches of frame H, are ttached to A and to the tube V, which connects the measuring-ube M and the levelling-tube D. The blocks *z* are connected y iron strips *m* with the loops *w*, by means of which they can e easily and safely put in any of the notches of the frames H. he tube *a*, placed at the bottom of bulb A, is connected with by a thick india-rubber tube.

Inside bulb A is the combustion-tube *g*, which is shown on larger scale in Fig. 58. It consists of a nickel tube, in which nickel wire *v*, insulated by a glass tube, is fixed. The tube and the wire are at the top connected by a platinum-wire spiral. The bottom end of this tube projects outside the bulb A, and the wire *v* is provided with a screw clamp, for connecting it with the source of electricity. In order to keep the platinum wire at an even temperature, and thus to prevent it from fusing by excessive heating, an adjustable resistance should be placed in the circuit to regulate the current. Three Grove cells will keep the spiral red-hot for one and a half to two minutes, which is sufficiently long for a combustion to be completed. If the platinum wire turns bright red, the resistance should be increased to prevent it from getting still hotter and ultimately fusing.

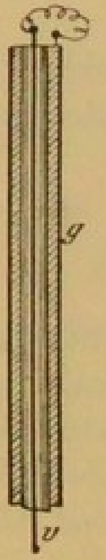

FIG. 58.

The tubes attached to the measuring-tube M and the laboratory vessel A are connected at *v* by rubber tubing and brass clips (the distance between *v* and *d* is somewhat greater than represented in the figure); *d* and *n* are three-way taps, and *h* a simple straight-bore tap, which should be from 12 to 15 mm. thick to insure its keeping tight.

To introduce the gas sample tube *g* is drawn down to the bottom of bulb A, and A, M, and D are filled with mercury by raising bulbs F and L; the taps *d* and *h* are then closed, and the gas is syphoned into A through the three-way tap *d*, by turning it so as to connect the gas supply with A. If the gas is to be drawn from a sealed bulb, this is attached to the rubber tube connected with tap *d*, and the end broken inside the tubing; the other end is broken off under mercury, in a suitable containing vessel, and the gas is drawn into A by lowering the pressure bottle F, after turning tap *d* so as to make connection with A. Now taps *d* and *h* are turned 90°, and, by raising bulb F and lowering L, the necessary quantity of gas is forced into M. Any excess of gas or any liquid remaining in A is removed by opening tap *d*, so as to make connection with the outside air. After reading the exact volume of the gas in M, 0·3 to 0·5 c.c. of potassium hydroxide solution are introduced through the funnel *t* into A, for the absorption of carbon dioxide. The gas is then transferred from M into A, and after the absorption syphoned back to a mark just in front of tap *d*. The volume of he connecting capillary tube up to this mark must be ascer-ained in the calibration of M, and allowed for. For the bsorption of oxygen, 0·1 c.c. of a 1 : 3 pyrogallol solution is imilarly introduced into A, where it already finds the necessary potash solution, and the volume of the gas now remaining is gain measured in M. (In ordinary producer-gas, etc., there is frequently no oxygen whatever, so that the volume of the gas emains unchanged in this operation.)

After the determination of CO_2 and O, the bulb A must be thoroughly cleaned before burning the hydrogen, carbon monoxide, and methane, because otherwise some of the carbon dioxide formed by this operation would be at once retained by the caustic liquor present. For this purpose A is washed out two or three times with 10 to 20 c.c. of water, which is ntroduced through the funnel *t*, and expelled through the tap *d*. If by mistake any of the absorbent has got beyond *d*, or nto tube M itself, it is removed by first clearing the air out f A, syphoning water from A into M, and then drawing back he gas and liquid into A, until the mercury reaches *d*; the as is then syphoned back into M, and the wash-water expelled s before through *d*.

The combustion of hydrogen, hydrocarbons, and carbon monoxide is effected by drawing the necessary quantity of ir or oxygen into tube M. For 100 parts producer-gas sually 120 parts of air; for 100 semi-water gas 150; and for 00 water-gas 350 parts of air is sufficient. If, for instance, M holds 120 c.c., it should not receive more than 50 c.c. of roducer-gas, to which now 60 to 70 c.c. air is added; and in he case of water-gas, only 25 c.c. of it may be used with about 0 c.c. of air. As this quantity of gas is too small for accurate eterminations, it is better in the case of water-gas to employ n lieu of air a mixture of 35 c.c. of air and 25 c.c. of oxygen or 40 c.c. of water-gas. It is preferable to burn this mixture n successive portions of about 30 c.c. at a time, rather than ltogether, especially if the worker has no experience with he apparatus; also, it is advisable to effect the combustion nder slightly reduced pressure.

The oxygen can be generated in a small tube of the orm shown in Fig. 59. About 2 g. of potassium chlorate are eated in this tube, which is attached by *a* to the rubber connection of the tap *d*, Fig. 57. After the contained air has been cleared out through *e*, which is placed under water, the taps *d* and *n* are opened to first clear out the capillary tube with oxygen; *n* is then closed and the oxygen introduced into A by lowering F.

The gaseous mixture is again allowed to go back into M, and once more over the hot platinum wire into B, and is ultimately measured in M, thus ascertaining the contraction caused by the combustion. Now the carbon dioxide formed is determined in the manner mentioned on p. 96, afterwards the oxygen in excess, and thereby all the figures are obtained for calculating CO_2, CO, CH_4, H, O, and N.

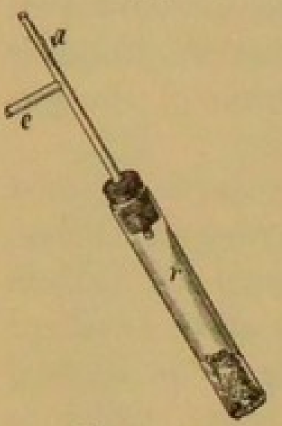

FIG. 59.

If scientifically accurate results are to be obtained with this apparatus, the tubes M and D are graduated in millimetres, and readings taken of the barometer, the height of the columns in M and D, and the temperature of the water in the jacket round M, at each observation during the analysis. The volumes are then reduced to 0° and 1000 mm. pressure by the formula:

$$V = \frac{v(B - b - e)}{1000[1 + 0{\cdot}00366t]},$$

in which v is the volume of gas read off, B the height of the barometer (reduced to 0°), b the difference of level between M and D, and e the tension of aqueous vapour at the temperature t of the experiment. By adjusting the columns of mercury in M and D to the same level after each determination, the correction for pressure is avoided; the correction for temperature is only required in cases where special accuracy is called for, since the changes of temperature in case of a water-jacketed measuring-tube are, as a rule, but slight during the interval of an analysis.

The calculation of the proportion of hydrogen, carbon monoxide, and methane follows from the volumetric changes according to the equations:

$$H_2 + O = H_2O;\ CO + O = CO_2;\ CH_4 + 2O_2 = CO_2 + 2H_2O.$$

The contraction in the case of hydrogen (w) is $= \frac{3}{2}$; in the case of carbon monoxide (c) $= \frac{1}{2}$, and in that of methane (m) $= 2$; both carbon monoxide and methane in combustion yield their own volume of carbon dioxide. Taking V as the total volume of combustible gases, n as the total contraction, and k as the total carbon dioxide formed, the resulting equations are :—

$$V = w + c + m\,;\ n = \frac{3}{2}w + \frac{1}{2}c + 2m\,;\ k = c + m.$$

Or,

$$\text{Hydrogen } (w) = V - k.$$

$$\text{Carbon monoxide } (c) = \frac{1}{3}k + V - \frac{2}{3}n.$$

$$\text{Methane } (m) = \frac{2}{3}k - V + \frac{2}{3}n.$$

The following is an example of the analysis of a producer-gas.

Volume of gas taken, 60 c.c.

After absorption of carbon dioxide, 56·1; therefore 3·9 c.c. carbon dioxide.

After addition of air, 116·1; therefore 60 c.c. air containing 47·4 c.c. nitrogen has been added.

After combustion, 101·2; therefore $n = 14·9$.

After absorption of carbon dioxide, 87·6; therefore $k = 13·6$.

After absorption of oxygen, 85·7.

Of this nitrogen, 47·4 added as air; therefore 38·3 c.c. nitrogen and $V = (56·1 - 38·3) = 17·8$.

Hence :—

Volume of hydrogen $= 17.8 - 13.6 = 4.2$ c.c.
,, carbon monoxide $= 4.5 + 17.8 - 10 = 12.3$ c.c.
,, methane $= 9·1 - 17.8 + 10 = 1.3$ c.c.

and the composition of the producer-gas :—

Carbon dioxide . .	3·9	c.c. or	6·5	per cent.
Hydrogen . . .	4·2	,,	7·0	,,
Carbon monoxide . .	12·3	,,	20·5	,,
Methane . . .	1·3	,,	2·2	,,
Nitrogen . . .	38·8	,,	63·3	,,
	60·0	c.c. or	100·0	per cent.

APPARATUS OF DREHSCHMIDT.

In this apparatus (described in *Berl. Ber.*, 1888, pp. 3242 *et seq.*; *J. Gasbelucht.*, 1889, p. 3) mercury is employed as confining liquid; the variations of temperature and pressure are compensated by the arrangement proposed by Petterson (*Z. anal. Chem.*, xxv. p. 467), already mentioned *suprà*, p. 21, and also employed in some of Hempel's gas-analytical apparatus. Drehschmidt describes his apparatus as follows:—

The tap *b* attached to the top of the burette B possesses a peculiar bore, shown in the enlarged drawing at the side, which allows of connecting B with the capillary tubes attached to each side, one of which (that which is turned upwards) leads to the differential pressure gauge M; the other capillary can be connected by means of a rubber tube with a pipette. Moreover, M can be connected by the tap *b* with the upright tube on that tap, and thereby with the air outside. C is the compensating tube; it is at the top provided with the tap *a*, the peculiar bore of which (visible in the enlarged side figures) enables C and M either to communicate with each other, or with the outside air, or to be both shut. The pressure gauge M, containing a drop of coloured liquid (either dilute sulphuric acid or high-boiling petroleum) is tightly joined by rubber tubes with the two lateral, vertically turned-up tubes belonging to the taps *a* and *b*. C, B, and M are held by the clip *k*. At the bottom the burette B is continued into a rubber tube with the screw clamp *f*, followed by a simple tap *e*. From the latter a thick rubber tube leads to the levelling bulb N, filled with mercury. The water jacket surrounding B and C contains a stirring arrangement, consisting of a copper wire with a suitably cut-out plate, which is moved up and down before taking readings in order to equalise the temperature. A drop of water is introduced both into B and C, so that the enclosed gases are saturated with moisture.

The burette B is provided with a millimetre scale, 600 mm. long, and its contents from tap *b* down to the lowest point of the scale is put = 100 vols., which space must be calibrated with mercury, so that the space value corresponding to each mark of the graduation can be entered into a table to be used for all further measurements. For this and all further readings the eading-microscope of Schmidt and Haensch, in Berlin, is ecommended.

In order to measure off exactly 100 vols., the gas is spirated into the burette a little beyond the end of the scale,

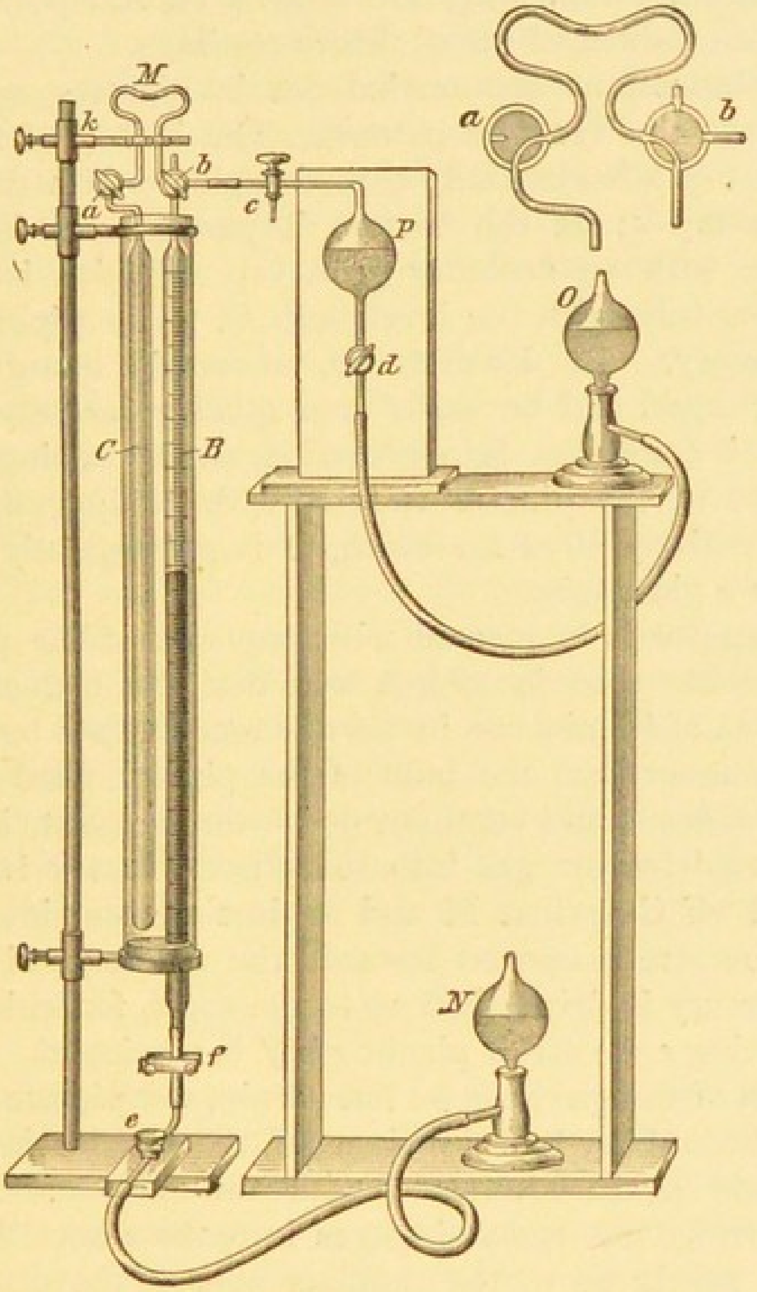

FIG. 60.

nd is then connected by turning tap *b* with its upper and ight-hand side tube. But raising N, the mercury is forced up early to the mark 600; then shut *e*, stir the water in the acket round C and B, and take off the surplus pressure by a rief opening of *b*. By means of the pinchcock *f* bring the ercury up to exactly the mark 600. Remove the slight over-pressure of the gas by a momentary opening of *b*, and then turn this tap so that B communicates with M. Proceed in the same way with the compensating tube C, which before had been in communication with the outside air. The index in M, which is about 5 mm. long, now takes a certain position, which must be re-established for all future readings.

The absorptions are carried out in pipettes, which differ a little from the Hempel pattern. The bulb P of the pipette has at the top a horizontally turned capillary with the capillary three-way tap *c*; at the bottom it passes over into a wide glass tube with an ordinary glass tap *d*, which is connected by a rubber tube with the level bulb O. The pipette is filled with mercury. By lowering O, a certain quantity of the absorbing liquid can be easily and quickly introduced by the tailpiece of *c*, and can be removed again by raising O. Only in the case of the pipette charged with fuming oil of vitriol, which is entirely filled therewith, O is permanently connected with P by a glass tube.

The burette is connected with any one of the pipettes by a short rubber tube in such a way that the two ends of the outlet tubes of *b* and *c* are in narrow touch, tap *c* being turned in such manner that the bulb of the pipette, filled up to this tap with a few cubic centimetres of the reagent, is shut off. In order to drive the gas into the pipette, first *a* is turned so as to shut off C against M and against the outside air; only then the burette is opened towards the pipette, and by raising N the mercury is driven just up to the tap *b*, for which purpose after shutting *e* the screw pinchcock *f* is employed. When the absorption of the gas goes on but slowly, the pipette is shut off by tap *c*, the rubber joint is taken off, the pipette is vigorously shaken and again connected with the burette. When on retransporting the remaining gas into the retort the reagent has risen nearly up to the capillary part of the pipette, tap *d* is shut so far that the rising can take place but slowly, and it is entirely shut when the liquid has got up to *c*. Now bulb N is raised so high that the mercury level therein is at the same height as that in the burette, and tap *c* is closed. If now a connection is established between B and M, the index in M is shifted a little; by means of the screw clamp *f* it is brought back again, and M and C are also put into communication.

in consequence of this, and of the stirring of the water in the water jacket, mostly the index is again shifted. It is brought into its original place by means of *f*, and the reading is now taken.

Combustions of gases are made by Drehschmidt's platinum capillary which has been already shown *suprà*, p. 92, Fig. 56, in connection with the Hempel apparatus. So much oxygen or air is mixed with the gaseous remainder, or a measured part of it, that there is an excess of oxygen present. From the contraction and the carbon dioxide formed, the original proportion of hydrogen and methane is calculated as shown on pp. 98 *et seq.*

Mathers and Lee (*Chem. Eng.*, 1913, xvii. p. 161) modify the Drehschmidt capillary by filling a quartz tube with pieces of platinum wire, closing both ends with pieces of wire netting, and placing the tube between a mercury pipette and a mercury burette. The burette contains the gaseous residue and the oxygen. The combustion takes three minutes; the results are exact. The expansion of the gas in heating must be allowed for by taking notice of the temperature in reading off the volume, and of the volume of the tube in which a little carbon dioxide remains at the end.

A simple form of gas-analysis apparatus, in which mercury is used as the confining liquid, has been described by W. A. Bone and R. V. Wheeler, in *J. Soc. Chem. Ind.*, 1908, xxvii. p. 10.

PFEIFFER'S APPARATUS.

This apparatus is specially intended for the analysis of coal-gas, and is described in *J. Gasbeleucht.*, 1899, xlii. p. 209; it is supplied by H. Hörold, glass-blower, Magdeburg.

Since the errors that may arise in the estimation of carbon monoxide by cuprous chloride are not altogether overcome by using a second absorption pipette, since a partial absorption of the residual gases other than carbon monoxide may possibly occur, Pfeiffer is of opinion that it is both simpler and more accurate to estimate the carbon monoxide by explosion, together with the determination of the hydrogen and methane. From his experience he also regards it as preferable to oxidise the hydrogen and methane together, rather than to adopt the method of fractional combustion. From these considerations the course of analysis adopted consists in the successive estimation of the carbon dioxide, heavy hydrocarbons, benzene, ethylene, oxygen, by absorption methods, and the combustion of hydrogen, carbon monoxide, and methane by explosion in one operation, as described in connection with F. Fischer's apparatus (*suprà*, p. 95). Thus the lengthy and not very reliable absorption of carbon monoxide, as well as the fractional combustion of hydrogen and methane are done away with. By estimating the carbon dioxide formed, the total contraction and the residual nitrogen, the necessary data for calculation on the lines described on pp. 98 and 99 are obtained. A complete analysis of coal-gas can be carried out by this method in three-quarters of an hour, which is of great advantage for the accuracy of the results. Since the heavy hydrocarbons present in the form of vapour and of gas are separately estimated, the analysis permits also of calculating the illuminating value of the gas.

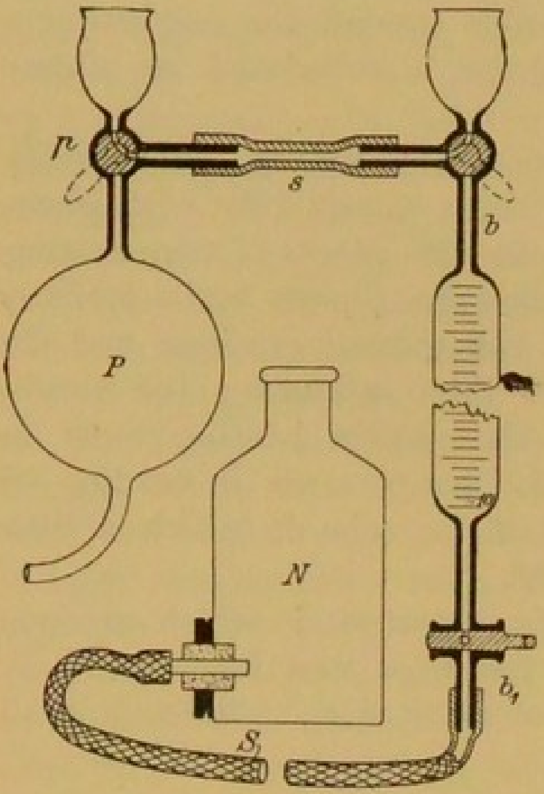

FIG. 61.

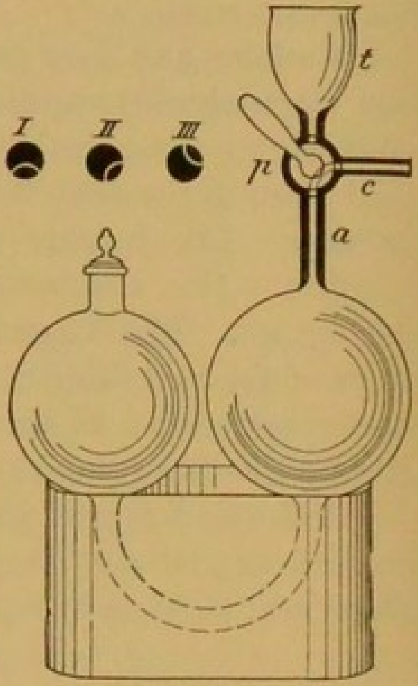

FIG. 62.

The apparatus consists of the burette and levelling flask, Fig. 61, two or three absorption pipettes, Fig. 62, a phosphorus pipette, and an explosion pipette, Fig. 63.

The burette B is provided with a stopcock *b* and funnel, and is attached to the pipette P as shown; its capacity is 100 c.c.; its lower end is connected by the rubber tube S with the levelling bottle N, holding 300 c.c. The confining liquid is water, acidified with 0·5 per cent. of sulphuric acid, which addition prevents the absorption of carbon dioxide, and takes up ammonia vapour after the absorption of the hydrocarbon vapours.

An improved form of burette, designed by Pfeiffer specially for the analysis of coal-gas, is shown in Fig. 64, and as arranged for the explosion of the combustible gases in Fig. 65. The bulb R at the top of this burette is connected by a narrow tube to the lower bulb; a mark *m*, made on the connecting tube, serves for measuring off the gas residue taken for combustion. The total capacity of the burette between the two stopcocks is sufficient to admit of employing the volume of air requisite for the combustion of the gas residue. The relative capacity of the two spaces, for coal-gas and for carburetted water-gas, should be about 1 : 5. The exact capacity of the burette up to *m* (= R), also the total capacity, J, and the volume of nitrogen contained in J when filled with air = N_1, are marked on the burette by etching, as shown in Fig. 64. Hence this burette permits the exact measurement of the gas residue and of the air which are successively passed into the explosion pipette.

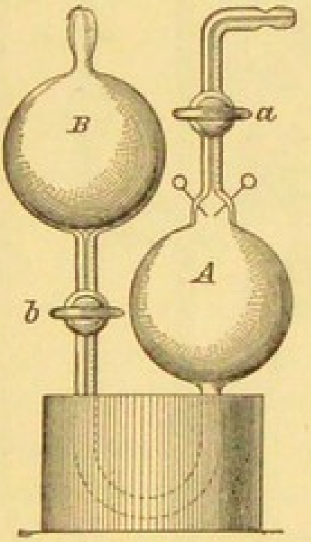

FIG. 63.

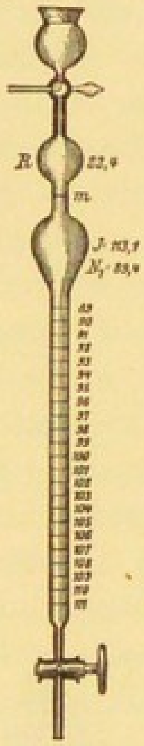

FIG. 64.

Owing to the form given to this burette, that part of it which serves for the measurements can be kept narrow enough to be provided with a division marking 0·1 mm. The zero point is just above bulb R, below the capillary, because the latter is filled with water after re-conducting the gaseous remainders into the burette. Only in the first measurement of the gas this is not the case, wherefore in this the contents of this capillary, say for example 0·2 c.c., must be taken into account, as will be explained *infrà*.

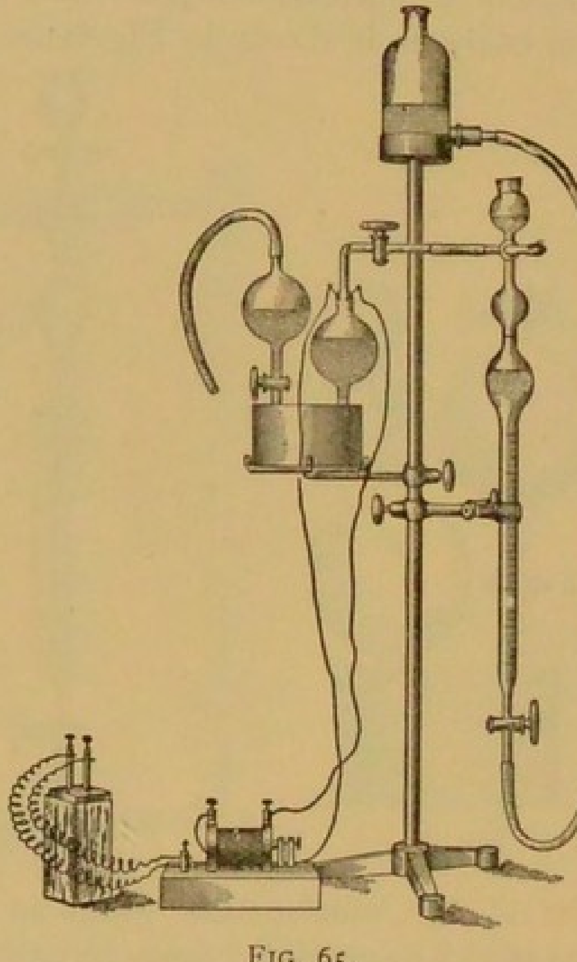

FIG. 65.

In lieu of the Hempel absorption pipette, Pfeiffer employs the modified form shown in Fig. 62, which permits of the replacement of the gas in the capillary connecting tube by means of water. The figure shows the capillary side-tube at *c*, which is connected with the burette; by altering the position of the stopcock *p*, in the manner which can be readily understood from the diagram, water may be run from the funnel *t* into the capillary *c*, and the air expelled before connecting with the burette; and when drawing the gas back to the burette after absorption, the absorbing liquid is allowed to rise only to the stopcock p; after which, by turning the latter through an angle of 90°, water is run from the funnel t into the capillary c, the gas remaining in which is thus forced into the burette; this operation is carried out before each reading. In place of the wooden or metal stand used by Hempel, the tube is bedded in a sheet-metal case by means of paraffin wax or plaster-of-Paris.

To take the sample of the gas, the burette B is first filled completely with water by raising the levelling vessel N, and opening the stopcocks b_1 and b (Fig. 61), and the sample is then drawn in by lowering N in the usual manner, until the volume of gas is a little below the zero mark; the stopcocks are then closed, and N is again raised. To measure off exactly 100 c.c., the lower stopcock b_1 is carefully opened, and the water allowed to rise to the true zero; the upper stopcock b is then momentarily opened, and the volume checked in the usual manner with the levelling bottle N. In the first reading the zero lies as much below the zero mark as is equivalent to the content of the capillary at b, since the latter is filled with water in the subsequent measurements, and the 100 c.c. graduation is at the lower end of the capillary. This correction (generally 0·2 c.c.) is therefore determined once for all as follows:—

Air is introduced into the burette to about the division 90, then water until the capillary at b is filled, the stopcocks are closed, and the reading taken after two minutes; meanwhile the water is completely removed from the capillary tube of the stopcock, the water then run out of the capillary into the burette and another reading taken; the difference between the two readings gives the capacity of the capillary. It is advantageous to use a meniscus screen, such as that of Göckel (p. 35) in taking the readings, so as to avoid parallax errors.

The single constituents of the gas are estimated as follows:—

Carbon Dioxide.—The pipette, Fig. 62, is filled up to the top with potassium hydroxide solution, and is connected with the burette as shown in Fig. 61. The stopcocks of both the burette and the pipette are turned to the position in which the two funnels communicate with each other; water is poured into one of them to expel the air from the connection b-s-p; the stopcocks of the burette and of the pipette are turned through 180°, and the gas is transferred from the burette into the pipette. While it is passing over, the contents of the pipette are shaken for a moment, so as to mix the water from the capillary connections with the alkali. As soon as the water reaches the stopcock *p*, the burette stopcock *b* is closed; the absorption is complete in one minute. The gas is then syphoned back into the burette by lowering the bottle N until the alkali reaches the stopcock *p* of the pipette, which is then turned through 180°, and the gas in the capillary *p-s-b* is washed out as before by means of the water in the pipette funnel. The burette stopcock *b* is then closed and the reading taken as usual, after allowing to stand for one minute.

Benzene Vapour.—This is absorbed with ammoniacal nickel cyanide solution; after shaking for three minutes (it is preferable to facilitate the shaking in this case by detaching the pipette), the residual gas is returned again to the burette, where the absorption of the ammonia vapours is effected by the acidulated water used as the confining liquid. As a check, about 0·5 c.c. of fresh acidulated water is introduced into the burette from the pipette funnel.

The ammoniacal solution of nickel cyanide, recommended for the estimation of benzene vapour by Dennis and M'Carthy, *J. Amer. Chem. Soc.*, 1908, xxx. p. 233, is prepared as follows:—A solution of 25 g. potassium cyanide in 25 c.c. of water is added to a solution of 50 g. of crystallised nickel sulphate in 75 c.c. of water, 125 c.c. of ammonia (sp. gr. 0·91) added, the whole cooled to 0°, and poured off from the separated potassium sulphate; a solution of 18 g. of citric acid in 10 c.c. of water is then added, the mixture again cooled to 0° for ten minutes, decanted from the potassium sulphate crystals, and a few drops of benzene then added and shaken till combination takes place, as the solution is much more active after it has absorbed some benzene. This solution has no action on ethylene or on carbon monoxide; the former may be estimated by absorption with bromine or fuming sulphuric acid after the removal of the benzene. The small quantities of benzene homologues present would not be absorbed by the ammoniacal nickel cyanide; but their amount rarely exceeds 0·1 per cent. Some contend that it is difficult to remove the ammonia from the remaining gas, ut Pfeiffer, as he states in Lunge-Berl's *Chem. Techn. Unt. Meth.*, ii. p. 238, did not confirm this.

Ethylene (or total heavy hydrocarbons, if the separate stimation of benzene vapour is not required) is absorbed by igorously shaking for three minutes with bromine water. The romine vapours are subsequently removed by forcing the aseous remainder into the potash pipette, manipulating just in he same way as if the gas had to be transferred into the urette. This is done by sucking at the open end of the potash ipette by means of a rubber tube. Then this pipette is onnected with the burette, and the reading made.

Oxygen is estimated in the phosphorus pipette (Fig. 51, . 85). The capillary space between the pipette and burette s cleared, by forcing the water from the pipette into the urette funnel by attaching a piece of rubber tubing to the pen end of the pipette and blowing.

Carbon Monoxide, *Hydrogen*, *Methane*, *and Nitrogen*.—The xplosion pipette, Fig. 63, is used for the estimation of these ases. In the analysis of coal-gas from 20 to 22 c.c. of the gas ft after absorption, which requires about five volumes of air r combustion, are first measured off in the burette, allowing he excess to escape; since, in doing so, the capillary at b is reed from water, its capacity, as determined, must be added to he reading. The burette and explosion pipette are then con-ected, the air in the connecting capillaries displaced as in the ase of the phosphorus pipette, and the gas passed over. The xplosion pipette is then disconnected and the burette filled ith air. The air is then transferred to the explosion pipette, he water allowed to rise as far as the bulb of the pipette, the topcock a then closed, and the small quantity of water remaining n the explosion chamber A withdrawn into the reservoir B, o that only the V-shaped connection remains filled with water; he stopcock b is then closed. An electric spark is then passed hrough the mixture in the usual manner, the pipette stopcock arefully opened so that the enclosed water comes back into the xplosion chamber quickly, and a little oxygen passed back nto the burette. The carbon dioxide formed in the combustion s then absorbed by potassium hydroxide, and the excess of xygen by phosphorus, whereby a direct measurement of the otal nitrogen, inclusive of that added as air, is obtained.

Calculation of the Results.—This takes place according to the following equations:—

$$H = V - CO_2.$$

$$CO = CO_2 + V - \frac{2}{3} C.$$

$$CH_4 = \frac{2}{3} C - V.$$

Here V signifies the combustible gases, C the total contraction after absorption with alkali.

The sequence of the separate readings and the resulting data are shown by the following example:—

Readings.		Data.	In residue R.	In 100 parts of gas.
A. ABSORPTION.				
Initial reading	100·0	...	...	...
After absorption with alkali .	98·3	...	...	CO_2 = 1·70
After absorption with nickel solution	97·27	...	...	C_6H_6 = 1·03
After absorption with bromine	94·48	...	...	C_2H_4 = 2·79
After absorption with phosphorus	93·7	...	...	O = 0·73
B. EXPLOSION.				
Gas residue taken (R) .	22·4	V = 21·55	H = 13·75	H = 57·51
Air added (J)	113·1	...	CH_4 = 6·05	CH_4 = 25·31
Reading after explosion .	101·9	C = 41·40	CO = 1·75	CO = 73·72
Reading after absorption with alkali	94·1	CO_2 = 7·80	...	...
Reading after absorption with phosphorus . .	90·25	N_1 = 89·40	N = 0·85	N = 3·56

VARIOUS APPARATUS FOR TECHNICAL GAS-ANALYSIS.

We here mention only some of the recently described apparatus, modifying those described *suprà*:—

Lomschakow (Ger. P. 251734).

Göckel (*J. Gasbeleucht.*, 1912, p. 1057).

Taplay (*J. Gas Lighting*, cxviii. pp. 217 and 285; cxxii. pp. 870 and 933).

Burrell (*J. Inst. Eng. Chem.*, iv. pp. 297 and 1445).

Eckardt (Ger. Ps. 241686 and 242315).

Egnell (B. P. 29211 of 1911).

Agraz (*Z. anal. Chem.*, 1913, p. 418; *Abstr. Amer. Chem. Soc.*, 1913, p. 3049).

Liese (B. Ps. 27467 of 1911; 23656 of 1912).

Einer Iohnson (Amer. P. 1074795).

Hayes (Amer. P. 1077342).

Kleine (Ger. P. 190240).

Siemens and Halske (Fr. P. 458916).

Arndt (B. P. 15019 of 1912; Ger. Ps. 241075, 242540, 242650).

Matzerath (Ger. P. Appl. M. 59308).

APPARATUS FOR THE RAPID AND CONTINUOUS ANALYSIS OF GASES.

During recent years various methods and many apparatus or a rapid and continuous testing of gaseous mixtures have come into use. Most of these are destined for the examination of fire-gases, or smoke-gases, or coal-gas, and we shall mention them later on in treating of these gases.

In this place we only mention the gas-analysis apparatus constructed by Simmance, Abady, & Wood, East Sheen, Surrey (B. P. 11664 of 1912), Ph. Eyer (Ger. P. 256218).

Harger (B. P. 9623 of 1912; *Abstr. Amer. Chem. Soc.*, 1912, p. 3255).

A. Schmid (B. P. 25046 of 1912).

Eynon (Amer. P. 1052412 of 1913).

Hüfner (B. P. 11679 of 1912; Ger. P. 247335).

Woodroffe and Boultbee (B. P. 5039 of 1912).

L. Sanders, Assignor to the Sarco Fuel Saving and Engineering Company, New York (B. P. 1683 of 1911; Amer. P. 055420).

Burrell and Seibert (*Bureau of Mines Tech. Pap.*, 1913, ol. 31, p. 1).

Davidson (described by Balcon in *J. Gas Lighting*, 1913, p. 102).

Bone and Wheeler (*J. Soc. Chem. Ind.*, 1908, p. 10).

Than (*Z. angew Chem.*, 1912, ii. p. 90).

Cross (Ger. P. 243603).

Hartung (Ger. P. 244859).

Knoll (Ger. P. 248318).

Lévy (B. P. 12841 of 1911).

Heckmann (Ger. P. 252538).

Arndt (Ger. P. 242540).

Martens (B. P. 11851 of 1911; Amer. P. 1060996; Ger. P. 234983).

Boulton (B. Ps. 5601 and 16300 of 1912; Amer. P. 1074795).

VARIOUS METHODS EMPLOYED IN TECHNICAL GAS-ANALYSIS.

I. ESTIMATION OF SOLID AND LIQUID ADMIXTURES (SOOT, DUST, ETC.) IN GASES.

The gases to be examined in the practice of chemical operations frequently contain solid or liquid substances, mechanically carried along, which cannot always be entirely retained by rest, filtration, or washing. The liquid admixtures are always accompanied by vapours of the same substance, if this is volatile.

Although in most cases the presence of such solids or liquids in a gas does not sensibly influence its volume, and hence has no influence on the results of gas-volumetric analysis, it is frequently desirable for general purposes to remove these impurities, and therefore methods are required for estimating their quantity. This is usually done when taking the samples of the gas for its analysis. Of course we must know the quantity of gas in question, and since for the purpose of estimating those impurities comparatively large quantities of gas must be employed, its quantity is generally measured by a gas-meter, or else by an aspirator worked by outflowing water. The meter or aspirator is always placed behind the gas-analytical apparatus.

Solid admixtures (*Cf.* Lunge-Keane's *Techn. Methods*, i. pp. 899 *et seq.*) in the case of smoke-gases, producer-gases, and analogous cases consist partly of soot, partly of minute particles of minerals, metals, coal, etc. In the flue-dust from metallurgical operations are found the oxides, sulphides, sulphates, chlorides, etc., of various metals.

The quantity of dust contained in a gas may vary between great limits. Thus Fodor found in the street air of Budapest, 15 ft. above the street level, on the average:

In winter . .	0·00024 g.	dust per cubic metre
„ spring . .	0·00035	„ „
„ summer . .	0·00055	„ „
„ autumn . .	0·00043	„ „

Tissandier found in the air of Paris, after a week's dry weather 0·0230, after heavy rain 0·0060 g. dust per cubic metre. Hesse found in a cubic metre of air from a living-room and nursery 0·0016 g., from the rag-picking shed of a paper work 0·0229 g., from the cleaning-room of a foundry 0·1000 g. dust. Stapff found in a cubic metre of air from the St Gothard Tunnel, during the time it was constructed, 1·900 g. dust; Theisen in the same, before washing the air 3·340 g., after washing 0·010 g. dust. Scheurer-Kestner found in chimney-gases from a coal fire, when strongly firing 0·2209, when damping the fire 0·9649 g. carbon as soot. Krause found in 1 cbm. of air from a match factory 0·004 to 0·005 g. phosphorus.

Large quantities of air must be employed for estimating the dust, if not merely its quantity is to be ascertained, but a microscopical and chemical examination is to be made for determining its hygienic properties, or its value, or its inflammability. The latter exerts great influence in the case of explosions in coal pits and flour mills.

The retention of solid substances mixed with a gas in the shape of dust is performed by *filtration*. Even very small particles, down to about 0·0002 mm. diameter, such as they occur, *e.g.* in coal smoke, can be retained by employing a suitable filtering medium, a sufficient filtering surface, and a not over rapid current of gas. Carded cotton-wool is very efficient, but is not adapted to filtering air in the presence of acid gases. In this case gun-cotton or soft, curly glass-wool is employed. This material is placed in a so-called calcium chloride tube, and is dried by exposing the tube in an air- or water-bath at 100° to a current of dry air, until the weight remains constant. This tube is interposed between the place the air of which is to be examined and an aspirator or gas-meter. A suitable volume of gas, say about 1 cbm. per twenty-four hours, is drawn through the tube, which is then dried at 100°, and the increase of weight is ascertained. If the retained dust, which is principally found at the entrance end, is to be further examined, this can be done by the microscope and by the ordinary chemical methods.

The filtration of gases through filtering paper has been employed by Moeller, and has been worked out more fully by Rubner and Renk (*Arb. aus d. hygien. Inst. Dresden*, 1907; Hempel's *Gasanal. Methoden*, 4th ed., p. 123).

Friese recommends for this purpose the "blue-band" paper of Schleicher and Schüll, ordinary filtering paper not being sufficient for retaining all descriptions of dust.

O. Brunck employs for collecting the dust from the air of coal pits liable to contain fire-damp, filtering tubes provided with ground-on glass caps, which admit of weighing the dust with its natural moisture. These tubes are carried about in boxes lined with cork slabs, of such size that the caps cannot fall off.

Martens (*Stahl u. Eisen*, 1903, xxiii. p. 735) employs for the retention of dust, filtering paper extended between two metallic funnels and protected against tearing by a metal sieve placed on it.

Simon (*ibid.*, 1905, xxv. p. 1069) proposes for this purpose Soxhlet's ether-extraction capsules, dried before and after use at 105°.

Schroeder (*Z. für chem. Apparatenkunde*, 1907, ii. p. 458) first retains the coarse dust in two vertically placed brass tubes, nickel-coated inside, the second of which contains a cross wall; the fine dust is afterwards retained by a glass-wool filter.

Kershaw (*Rauch und Staub*, 1913, p. 193) describes some methods for estimating and registering the dust and soot in air.

The following class of apparatus is especially intended for ascertaining the quantity of *soot* in furnace-gases. Usually a known volume of these gases is drawn through a tube of refractory glass, containing a layer of asbestos, 20 cm. long. The soot retained here is afterwards burned in a current of oxygen, and the carbon dioxide absorbed in potash bulbs, in the same way as in elementary organic analysis, of course interposing a calcium chloride tube in front of the potash bulbs.

Several methods have been described for the *colorimetric* estimation of sooty matters in chimney-gases, etc. Thus

Fritzsche (*Z. Verein. deutsch. Ingen.*, 1897, p. 885) describes a test, founded on the more or less pronounced grey colour of a filtering medium, consisting of cellulose fibre, which is afterwards shaken up with a certain volume of water, and compared with the colour of paper tinted by Indian ink.

H. Wislicenus (*Z. angew. Chem.*, 1901, p. 689) exposes the air of forests, suspected of being contaminated by sooty gases, to frames covered with thin calico, and compares the degree of blackening produced after a certain time with that of pure air.

Silbermann (Ger. P. 179145; *Z. für chem. Apparatenkunde*, 1907, ii. p. 1907) describes an apparatus, in which the degree of blackening by sooty gases is ascertained by the assistance of a selenium cell.

Strong (B. P. 20199 of 1912) describes an apparatus for detecting suspended matter in gases, especially those passed between insulated electrodes, by the change in the current.

Phillips (*Trans. 8th Intern. Congr. Appl. Chem.*, xxv. 711; *Abstr. Amer. Chem. Soc.* 1913, p. 2467) describes a special filter for this purpose.

Liquid admixtures in gases occur mostly in the shape of vapour, especially if the sample is taken in the hot state, and they would then be estimated by the processes for estimating gaseous substances, described elsewhere. In cooling, the liquid may be partially condensed, but this condensation is never sufficiently complete to admit of a quantitative estimation of the substance in question; it should be always combined with an absorbing or washing process, in order to ascertain the total quantity of the impurity.

Water (*moisture*) is estimated by absorption in a weighed calcium chloride tube. If the gas contains ammonia it is preferable to employ the drying agent employed by Stas, and later on by C. Frenzel (*Z. Elektrochem.*, 1900, p. 486), which is prepared by heating a mixture of 3 parts of finely divided copper and 1 part potassium chlorate in an iron crucible to a strong red heat. The estimation of moisture by physical methods ("hygrometry") does not enter into the scope of this treatise.

Mercury (of which Tanda found 0·00875 g. per cubic metre in the principal chimney of the Idria quicksilver works) is estimated by interposing a weighed tube, filled with gold foil, and reweighing after the passage of the gas. Kunkel's method will be described later on.

Sulphuric acid, occurring as such or as sulphuric trioxide, together with sulphur dioxide in gases from roasting ores, etc., is found by estimating the total acids (*vide infrà*) and subtracting the SO_2 found by titration in another sample.

The estimation of a number of other liquids which occur in gases, mostly in the shape of vapour, will be described later on when treating separately of these substances.

II. Estimation of Gases by Absorption.

A.—BY GAS-VOLUMETRIC METHODS.

The gas-volumetric estimation of a gas by absorption is an estimation by difference. It is performed by taking out of a known volume of gas the absorbable gaseous constituent by means of a suitable reagent, measuring the residual gas, and subtracting its volume from the original volume of gas.

In previous chapters we have described numerous *apparatus* for this purpose, such as the absorbing parts of the Orsat apparatus and its various modifications (p. 66), of Dennis (p. 76), of Hempel (p. 82), of Drehschmidt (p. 100), of Pfeiffer (p. 103), and we shall describe some others later on. A new apparatus for this purpose is described in the Ger. P. 270088 of the Drägerwerk.

In this place we shall treat of the *absorbing agents*, reserving, however, for a later chapter the description of such absorbents as are used only in special cases. In preceding chapters we have already had frequent occasion to speak of these agents, but in this place we shall describe them generally.

General Remarks.—The absorbing agents are mostly employed in the form of solutions, frequently in a concentrated state, especially where they have to be used over and over again. As a rule, it is preferable to use the same absorbing liquid continually, nearly up to exhaustion, in order to diminish the error caused by the mechanical solubility of gases not intended to be retained, and not absorbed by a chemical reaction. When employing a freshly prepared absorbing liquid, this mechanical solution may take place to quite a sensible extent, leading to incorrectly high results for the gas to be chemically absorbed on purpose; this error does not take place when the liquid has been saturated with the mechanically dissolved gases.

It must not be overlooked that the absorbing agents mechanically dissolve some of the gases supposed to pass quite unchanged through them. This causes, however, too slight a fault to be worth noticing in technical gas-analysis, where consecutive analyses are made by means of the same apparatus used for many single analyses.

(a) *Absorbents for Carbon Dioxide.*

The general absorbent for this purpose is a solution of *potassium hydroxide*, which retains the CO_2 easily and rapidly. The ordinary solution is prepared by dissolving 250 g. of good commercial caustic potash, which need not be purified by means of alcohol, in water and diluting the solution to 800 c.c. One c.c. of this liquor contains about 0·21 g. real KOH, and consequently absorbs 0·083 g. = 42 c.c. CO_2. The absorption is finished in one minute or even more quickly; it is quite unnecessary to wait for it any longer, as some have recommended.

In some cases more or less concentrated potash solutions are employed. Where the contact between the gas and the absorbent cannot be increased by shaking, stronger solutions should be employed. For Bunte's burette, *e.g.*, the liquor need not be quite so concentrated, but for the Orsat apparatus it may be used in a more concentrated state. The higher its concentration, the greater is its viscosity and its chemical action on the glass of the vessels employed. *Caustic soda* has an even greater action on glass, and is therefore less recommendable for the present purpose, although it is cheaper than potash. *Barium hydroxide* is used in the examination of air by Pettenkofer's method and its congeners.

Of course these solutions absorb also other acid gases, as chlorine, hydrogen chloride, hydrogen sulphide, sulphur dioxide, etc.

(b) *Absorbents for Heavy Hydrocarbons.*

The heavy hydrocarbons occurring in technical gas-analysis are:—*Olefins*, of the general formula $C\,H_{2n}$, especially *ethylene*,

C_2H_4, *propylene*, C_3H_6, and *butylene*, C_4H_8; then the hydrocarbons of the series C_nH_{2n-2}, of which *acetylene*, C_2H_2, is the principal member coming into question; and the hydrocarbons of the *benzene* series, C_nH_{2n-6}, of which *benzene*, C_6H_6, and *toluene*, C_7H_8, are the most important. These hydrocarbons are the principal illuminating constituents in coal-gas, whence their estimation in this gas is of great importance, but not to the same extent as before the introduction of the Welsbach light. The absorbents for them in gas-analysis are:—

1. *Fuming Sulphuric Acid*, of sp. gr. about 1·938, and containing about 20 to 25 per cent. "free" SO_3.—It should be borne in mind that this reagent must be kept and employed at temperatures above 15°, because below this some pyrosulphuric acid crystallises out. It absorbs all the heavy hydrocarbons coming into question here, if agitated for five minutes with the gas. Hereby ethylene is converted into ethionic acid, $C_2H_6S_2O_7$, acetylene into acetylene-sulphuric acid, $C_2H_4SO_4$,[1] benzene into benzene-sulphonic acid, $C_6H_6SO_3H$.

The absorption is carried out in a simple Hempel gas-pipette (Fig. 47, p. 82), of course using all proper precautions in filling it; in order to prevent the attraction of moisture, it is closed by a small glass rod enlarged at one end, or by a glass cap, neither of which parts of apparatus need be taken off during use. Hempel prefers providing this pipette with an additional bulb above the ordinary one, filled with bits of glass, in order to enlarge the absorbing surface and to render agitation unnecessary (*cf.* Fig. 50, p. 85).

After treating the gases in the pipette charged with fuming sulphuric acid, they must be freed from acid vapours by means of a potash pipette.

Worstall (*J. Amer. Chem. Soc.*, xxi. p. 245) has observed that fuming sulphuric acid on prolonged contact absorbs a little methane and ethane, but no sensible error is caused by this, if the time of absorption is not extended over a quarter of an hour.

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[1] J. Schroeder (*Ber.*, 1898, p. 2189) states that fuming sulphuric acid with acetylene does not form acetylene-sulphuric acid but methionic acid, $CH_4S_2O_6$; but this cannot be correct, since it would involve the formation of carbon monoxide, which does not take place, as confirmed by Knorre and Arendt (*Verh. Gewerbfl.*, 1900, p. 166).

By this method only the total quantity of heavy hydrocarbons in gases can be estimated; methods for estimating some of them separately will be mentioned in a subsequent chapter.

2. *Bromine Water.*—This is a saturated solution of bromine in water, with a small excess of bromine. Here also, after employing the reagent, the gas must be treated with potash solution, in order to remove the bromine vapour. The reagent is kept in a composite Hempel pipette, Fig. 52, p. 86, provided with a water-seal. It quickly absorbs *ethylene* and its homologues, transforming them into bromides, without the necessity of agitation. Treadwell and Stokes (*Ber.*, 1888, p. 3131) and Haber and Oechelhäuser (*ibid.*, 1896, p. 2700) have found the absorption to be complete. *Acetylene* behaves like ethylene. *Benzene* is also absorbed, but according to Winkler (*Z. anal. Chem.*, 1889, p. 285) slowly and incompletely. Haber and Oechelhäuser (*loc. cit.*) found that benzene is not removed by chemical action of the bromine, but mechanically; if benzene vapour and bromine vapour are in contact during two minutes in diffuse daylight, no bromine is consumed. Hence ethylene and benzene cannot be separated by a simple treatment with bromine water; but if titrated bromine water is employed, the quantity of ethylene present can be ascertained by estimating the bromine consumed for the formation of ethylene bromide, no such consumption being caused by the benzene. They first ascertain the total quantity of heavy hydrocarbons by means of fuming sulphuric acid, and treat a second sample of gas with titrated bromine water, retitrating the unconsumed bromine by means of potassium iodide and sodium thiosulphate.

(c) *Absorbents for Oxygen.*

Only a few of the numerous reagents, proposed for the absorptiometric estimation of oxygen, have in the long run proved satisfactory.

The following substances can be recommended as thoroughly tested:—

1. *Phosphorus.*—White (yellow) phosphorus is moulded into thin sticks by melting it in a glass cylinder under warm water so as to form a layer 10 or 15 cm. deep, dipping into this a

glass tube of 2 or 3 mm. bore, closing this at the top with the finger, and quickly transferring it into a vessel filled with cold water. When the phosphorus solidifies, its volume shrinks so that the stick can be easily pushed out under water, especially if the glass tube is slightly conical. These thin sticks are cut into smaller sticks under water. Phosphorus moulded in this shape can also be obtained from the dealers in chemicals.

The phosphorus sticks are placed in a suitable vessel, *e.g.*, a Hempel's tubulated pipette, Fig. 51, p. 85, where they are completely covered with water and protected against light. The water serves as a seal; it is driven out by the gas to be examined, which thus comes into contact with the moist phosphorus, and the absorption of oxygen begins at once with formation of white clouds of phosphorous acid, which render the gas opaque for some time without influencing its volume. If this process takes place in a dark room, it produces a bright light; the vanishing of this, and the clearing away of the cloud, marks the end of the process. Generally a quiet contact of the gas with the phosphorus for two or at most three minutes is sufficient. One g. phosphorus on being transformed into phosphorous acid takes up 0·77 g. = 538 c.c. oxygen; hence the stock of phosphorus contained in an absorbing-vessel generally lasts for years; but the water covering it, which dissolves the phosphorus and phosphoric acid formed, must be renewed from time to time.

The following conditions must be observed in the employment of this reagent :—

(a) *Temperature.*—The absorption should be carried out between 15° and 20°. Below 15° it proceeds too slowly, and at 7° it ceases almost entirely.

(b) *Partial Pressure of Oxygen.*—Pure oxygen at the pressure of an atmosphere is not absorbed by phosphorus at temperatures below 23°. The absorption commences only when the gas has been reduced by means of the air pump to about 75 per cent. of the initial pressure; it may then set in with extreme violence, or even explosively, with the production of scintillations and the fusion of the phosphorus. If, therefore, a gas rich in oxygen, *e.g.*, commercial compressed oxygen itself, has to be examined, it should be diluted with its own volume of pure nitrogen (which may be taken out of a phosphorus pipette filled with air) or pure hydrogen. This should be done with all gases containing upwards of 50 per cent. oxygen.

(c) *The Presence of Certain Gases and Vapours* retards or even stops in a hitherto unexplained way the absorption of oxygen by phosphorus. (Perhaps this phenomenon is analogous to the "paralysing" action of minute quantities of hydrogen sulphide, carbon disulphide, and some other substances on the catalytic action of platinum and of organic ferments, as observed by Bredig and Müller von Berneck (*Z. physik. Chem.*, 1899, p. 324). Among the substances interfering with the absorption of oxygen by phosphorus are, according to Davy, Graham, and Vogel, hydrogen phosphide, hydrogen sulphide, carbon disulphide, sulphur dioxide, iodine, bromine, chlorine, nitrogen peroxide, ethylene, acetylene, ether, alcohol, petroleum, oil of turpentine, cupione, creosote, benzene, ammonia, alcohol, tar, and many essential oils. As little as $\frac{1}{1000}$ vol. PH_3, $\frac{1}{400}$ vol. C_2H_4, $\frac{1}{4444}$ vol. oil of turpentine suffice for producing this effect, and render the application of phosphorus impossible in such cases. But, according to experiments of Brunck, these disturbing substances can in most cases be removed by a previous treatment of the gas with fuming sulphuric acid, and after this the gaseous mixture, *e.g.*, coal-gas or fire-damp, may be treated by phosphorus for the absorption of oxygen. This proves the incorrectness of some statements according to which methane and ethane belong to the class of substances interfering with the absorption of oxygen by phosphorus, since methane and ethane are not removed by fuming sulphuric acid.

This method renders excellent service in the examination of air, of chimney-gases, of vitriol-chamber gases, etc., and as to certainty and speed of action, phosphorus is superior to every other reagent. Lindemann (*Z. anal. Chem.*, 1879, p. 158) has constructed a special apparatus for this purpose, which will be described in a subsequent chapter.

(d) *The Presence of Combustible Gases.*—According to Baumann (*Ber.*, 1883, p. 1146) and Leeds (*Chem. News*, xlviii. p. 25), carbon monoxide in the presence of oxygen in contact with moist phosphorus is partially oxidised into carbon dioxide. Remsen and Keiser (*Amer. Chem. J.*, 1883, p. 454) contradict this, but Baumann (*Ber.*, 1884, p. 283) maintains his former statement. Boussingault (*Comptes rend.*, lviii. p. 777) has shown that during the slow combustion of phosphorus in gases containing oxygen, a small portion of combustible gases present, such as carbon monoxide or hydrogen, vanishes together with the oxygen; but this simultaneous combustion is comparatively slow and, at least in technical gas-analysis, causes no sensible error.

(e) *Action of Light.*—As previously mentioned, the absorption vessel filled with phosphorus must be kept in the dark. Otherwise the white surface of the phosphorus is covered by a thin layer of red phosphorus which interferes with the absorption of oxygen.

A solution of phosphorus in oil has been proposed as a gas-analytical absorbent of oxygen by Centnerszwer (*Chem. Zeit.*, 1910, p. 404). It is prepared by placing about 230 c.c. of castor oil in a 250 c.c. flask, dropping into the oil 3 g. of well-dried phosphorus, closing the neck of the flask with a stopper, heating it in an oil-bath to 200°, removing the flask from the bath, and vigorously shaking it until the phosphorus is completely dissolved. The reagent is employed in a Hempel's double-absorption pipette (Fig. 52, p. 86), and the gas is allowed to stand in contact with it as long as a glow can be observed. The results are correct also even with gas mixtures containing a large proportion of oxygen.

2. *Alkaline Solution of Pyrogallol.*—An aqueous solution of pyrogallol in contact with air changes very slowly, but on the addition of an alkali it rapidly absorbs oxygen and takes first a red, afterwards a deep brown colour. According to Liebig (*Ann. Chem. Pharm.*, lxxvii. p. 107), 1 g. pyrogallol, after addition of potash solution, absorbs 189·8 g. oxygen; according to Doebereiner (*Gilb. Ann.*, lxxii. p. 203; lxxiv. p. 410), on addition of ammonia, 266 c.c. oxygen. This agrees with the results obtained by Mann in Winkler's laboratory, where 1 g. pyrogallol, dissolved in 20 c.c. potash solution of sp. gr. 1·166, absorbed 265·2 to 278·7, on the average 268·9 c.c. oxygen.

The behaviour of pyrogallol was first utilised for the endiometric estimation of the oxygen in atmospheric air by Chevreul, in 1820, and was further investigated by Liebig. Weyl and Zeitler (*Ann. Chem. Pharm*, ccv. p. 255) showed that the absorbing action of pyrogallol is a function of the alkalinity f the solution, but that in too highly concentrated solutions f potassium hydrate the absorbing power is weakened, robably by partial decomposition of the pyrogallol. A solu- on of KOH of sp. gr. 1·05 was found suitable; solution of p. gr. 1·50 was too strong. Winkler's experiments have shown at a solution of caustic potash of sp. gr. 1·166, as employed or the absorption of carbon dioxide, is very suitable indeed, 50 g. pyrogallol are dissolved in 1 litre of it. One c.c. of this olution absorbs 13 c.c. oxygen. This absorption goes on ore slowly than that of carbon dioxide, but it is usually omplete within three minutes, if the gas and liquor are brought nto very intimate contact, and if the temperature does not fall elow 15°. The solution is kept in a composite gas-pipette, igs. 52 and 56, pp. 86 and 87.

Boussingault (*Comptes rend.*, lvii. p. 885) and Calvert and loëz (*ibid.*, pp. 870 and 875) have shown that during the xidation of the alkaline solution of pyrogallol a small quantity f carbon monoxide may be formed, more or less, depending on e energy of the absorbing process. Pure oxygen yields more O than oxygen diluted with nitrogen or otherwise. The ormation of CO is also favoured by the concentration of the bsorbent. From 100 vols. pure oxygen Boussingault obtained 4, 1·02, 0·40, 0·06; Calvert 1·99 to 4·00, Cloëz 3·50; from 00 vols. oxygen mixed with various proportions of nitrogen, oussingault obtained 0·40, Cloëz 2·59 vols. carbon monoxide. onsequently Boussingault states that, when employing this bsorbent in the analysis of atmospheric air, it may happen at the volume of oxygen is found 0·1 or 0·2, or even 0·4 per ent. below the truth. Vivian B. Lewes (*J. Soc. Chem. Ind.*, 891, p. 407) recommends employing the solution not more than our times, as it only then begins to yield carbon monoxide. He also recommends keeping it for twelve hours before use, ut he gives no reason for this. Contrary to all these state- ents, Poleck (*Z. anal. Chem.*, 1869, p. 451), when specially xamining this source of error in researches on the composition f air, could not find even traces of carbon monoxide formed by e employment of pyrogallol, and he therefore recommends it s perfectly reliable in the case of moderate percentages of xygen. The same observation is made in technical gas- nalysis; at all events the amount of CO evolved is too small to sensibly influence the determinations of oxygen by this method, except in the analysis of "pure" oxygen.

The alkaline solution of pyrogallol of course equally absorbs carbon dioxide, and this gas must therefore be previously removed before commencing the absorption of oxygen.

3. *Copper* (*Ammoniacal Cuprous Oxide*).—Those metals which form soluble ammonia compounds, like copper, zinc, and cadmium in contact with ammonia and oxygen, are transformed into the respective compounds with absorption of oxygen. Lassaigne and later on Hempel (*Gasanal. Methoden*, 1900, p. 142) have applied this behaviour for the estimation of oxygen. Copper is preferred to the other metals, because it dissolves without the evolution of hydrogen, and because it can be employed in the shape of thin wire gauze offering a large absorbing surface. A tubulated gas-pipette (Fig. 51, p. 85) is charged with small coils of such wire gauze and with a mixture of equal volumes of a saturated solution of commercial ammonium carbonate and of liquor ammoniæ, of sp. gr. 0·96. If a gas containing oxygen is introduced into such a pipette, the oxygen is absorbed without any agitation in less than five minutes. Probably at first a compound of ammonia with cuprous oxide is formed, which absorbs a further quantity of oxygen and thus yields a compound of ammonia with cupric oxide, which, in contact with the copper present in excess, is retransformed into the cuprous compound. This would mean that 1 g. copper can absorb 177 c.c. of oxygen.

The application of this absorbent has the advantage that copper moistened with liquor ammoniæ absorbs oxygen much more quickly than the alkaline solution of pyrogallol, and more conveniently, as there is no necessity for agitation. Its efficiency is nearly equal to that of phosphorus, and its advantage over the latter is that it is absolutely harmless and that it acts down to a temperature of $-7°$. But its use is restricted by the fact that it absorbs equally well carbon monoxide, which is present in many cases where the oxygen has to be determined. It absorbs also ethylene and acetylene, the latter with formation of red explosive copper acetylide. Before employing it, any carbon dioxide present must of course be removed.

Red-hot copper is used for the absorption of oxygen in the

"Copper Eudiometer" of Kreusler (*Wiedemann's Ann. N.F.*, vi. p. 537; Hempel's *Gasanal. Methoden*, 4th ed., p. 309).

4. *Sodium Hydrosulphite* (Franzen, *Ber.*, 1906, p. 2069).—This compound acts according to the following equation:—

$$Na_2S_2O_4 + O_2 + H_2O = NaHSO_4 + NaHSO_3.$$

Its absorbing value is very great; 1 g. of it absorbs about 128 c.c. oxygen. It is used in weakly alkaline solution in Hempel's absorbing pipettes, for which purpose Frenzel recommends a solution, prepared by mixing a solution of 50 g. commercial sodium hydrosulphite (cost price 2s. 6d. per kilogramme) in 250 c.c. water with 40 c.c. of a solution of 500 g. caustic soda in 700 c.c. water. For use in a Bunte burette a less concentrated solution is employed, consisting of 10 g. sodium hydrosulphite in 50 c.c. water, mixed with 50 c.c. of a 10 per cent. caustic soda solution.

The advantage of this reagent over phosphorus is that the substances which prevent the oxidation of phosphorus are without influence on the hydrosulphite. Its advantages over the alkaline solution of pyrogallol are the cleaner work, the greater cheapness, and the higher degree of action. It is also independent of the temperature, and it absorbs no carbon monoxide (*cf.* No. 3).

5. *Chromium Protochloride* is recommended by von der Pfordten (*Annalen*, ccxxviii. p. 112) as an absorbent for oxygen which does not act on hydrogen sulphide and carbon dioxide. It is prepared by heating chromic acid with concentrated hydrochloric acid to green chromium chloride, which is then reduced to protochloride by reducing with zinc and hydrochloric acid, filtered and run into a saturated solution of sodium acetate; red chromium acetate is precipitated which is separated by filtration, washed and decomposed by hydrochloric acid, air being excluded.

6. *Alkaline Solution of Ferrous Tartrate*, proposed by De Koninck (*Z. angew. Chem.*, 1890, p. 727), is less efficient than the other agents described here.

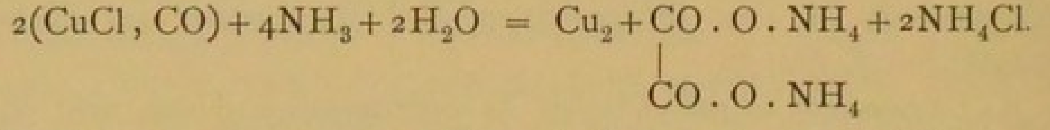
The absorbents employed for estimating oxygen in the form of *ozone* will be described later on when specially treating of that substance.

(d) *Absorbents for Carbon Monoxide.*

The general absorbent for carbon monoxide is a solution of *cuprous chloride*, CuCl, which combines with it to form carbonyl-cuprous-chloride. According to Manchot and Friend (*Annalen*, 1908, ccclix. p. 100), the process is:

$$\mathrm{CuCl + CO + 2H_2O \rightleftharpoons CuCl,\ 2H_2O,\ CO.}$$

Hence there is an equilibrium between the two sides of the equation, and the absorption of carbon monoxide by a hydrochloric acid solution of cuprous chloride, for which the above-given equation is valid, can never be complete. On the contrary, a long-used absorbing solution, which contains much of the copper-carbonyl-chloride, may yield up carbon monoxide by dissociation to gaseous mixtures containing but little carbon monoxide. For this reason it is generally preferred to employ the *ammoniacal* solution of cuprous chloride, with which the absorption of carbon monoxide is practically quantitative, as the easily dissociating cuprous-chloride-carbon-monoxide is continuously removed by a secondary reaction, by which ammonium carbonate and chloride and metallic copper are formed.



$$\mathrm{2(CuCl,\ CO) + 4NH_3 + 2H_2O = Cu_2 + \begin{array}{l} CO\,.\,O\,.\,NH_4 \\ | \\ CO\,.\,O\,.\,NH_4 \end{array} + 2NH_4Cl.}$$

The free copper protects the solution against oxidation and reduces any cupric chloride formed to cuprous chloride.

Pfeiffer (Lunge and Berl, *Chem. techn. Unt. Methoden*, 6th ed., 1911, iii. p. 239) prepares an *acid* solution by pouring 250 c.c. concentrated hydrochloric acid over 35 g. commercial cuprous chloride, placing some copper-wire net in the solution and keeping it protected from air until it has turned colourless. This solution is then poured into about 1·5 litre water, whereby white cuprous chloride is precipitated. After twenty-four hours the clear liquor above this is poured off and the cuprous chloride is dissolved in 250 c.c. liquor ammoniæ of sp. gr. 0·91.

Sandmeyer (*Berl. Ber.*, 1884, p. 1633) describes another way of preparing this solution. A very suitable solution of cuprous chloride, sufficiently ammoniacal, but with slight vapour tension, is prepared as follows:—250 g. of ammonium chloride is dissolved in 750 c.c. of water in a bottle provided with a good india-rubber cork, and to this is added 200 g. cuprous chloride; a metallic copper spiral, reaching from top to bottom, is inserted. The cuprous chloride dissolves on frequent agitation, leaving behind a little cupric oxychloride, and forming a brown liquid which keeps an indefinite time, if air is excluded. In contact with air a precipitate of green cupric oxychloride is formed. Before use, this solution is mixed with one-third its volume of liquor ammoniæ, sp. gr. 0·910. It is usually kept in Hempel pipettes with a water seal, provided at the lowest point of the connecting tube with a branch tube, fitted with a pinchcock, to facilitate the charging (Fig. 53, p. 87). The pipette is charged by connecting the open end of the pinchcock tube with a rubber tube reaching above the top of the pipette, putting a funnel into the tap, and pouring in at first 50 c.c. liquor ammoniæ and then 150 c.c. of the stock solution of cuprous chloride, whereupon the charging tube is taken off and the outer end of the pinchcock tube closed by a bit of glass rod.

One c.c. of this solution absorbs 16 c.c. carbon monoxide. But since this gas is held so loosely that the combination is destroyed to a slight extent even by a decrease of pressure, as found by Tamm (*Jernkontorets Annaler*, vol. xxxv.) and Drehschmidt (*Ber.*, 1887, p. 2752) the latter (*Ber.* 1888, p. 2158) recommends using two pipettes in series, the first of which is charged with a several times used solution of ammoniacal cuprous chloride, which absorbs the principal portion of the carbon monoxide present, whilst the second pipette contains a fresh and consequently very active solution of the same reagent which takes up the last traces of carbon monoxide. These two pipettes should be provided with labels of different colour, to prevent mistakes.

According to Gautier and Clausmann (*Comptes. rend.*, cxlii. p. 485 of 1906) the last traces of carbon monoxide cannot be removed in this way. They, as well as Nowicki (*ibid.*, p. 1186), recommend removing this small remainder of carbon monoxide by passing the gas over *anhydrous iodic acid* at 70°, and either estimating the CO_2 formed by passing the gas into baryta water, or estimating the iodine liberated by the reaction by titration with arsenious acid, or colorimetrically with potassium-iodide-starch solution in a solution in benzene or chloroform. This method is especially intended for proving the presence of traces of CO in atmospheric air.

The ammoniacal cuprous chloride solution absorbs also carbon dioxide, heavy hydrocarbons (especially acetylene and ethylene), and oxygen, all of which must therefore be removed before estimating the carbon monoxide.

The prescription for employing the ammoniacal cuprous chloride solution in the Bunte burette is: agitating the gas with it for one minute, drawing off the solution, replacing it by fresh solution, agitating again, and repeating this at least twice. After the last drawing off, run 3 to 4 c.c. concentrated hydrochloric acid from the funnel into the burette, then water which forms a layer on the acid, draw off the liquid, wash with water, draw in 1 to 2 c.c. caustic potash solution, agitate, allow water to enter, place the liquids on a level, and read off.

Czakó (*J. Gasbeleucht.*, 1914, p. 169) points out that the cuprous chloride solution should be colourless. No more than 5 c.c. of it should be put into the burette, without any violent shaking, and this must be twice repeated.

The application of this reagent to a qualitative and an approximate colorimetrical estimation of carbon monoxide will be mentioned later on.

(e) *Absorbents for Nitrogen.*

Such an absorbent is used for the isolation of argon and its congeners. Hempel (*Z. anorg. Chem.*, 1899, xxi. p. 19) has shown that nitrogen is absorbed at a red heat by a mixture of 1 part magnesium powder with 5 parts freshly ignited calcium oxide and 0·25 parts sodium. 1 g. of this mixture absorbed by an hour's contact 52 c.c. of nitrogen.

Franz Fischer (*Berl. Ber.*, 1908, p. 2017) showed that calcium carbide may be employed for the absorption of nitrogen, together with oxygen, leaving behind the gases of the argon group. An apparatus for this purpose, founded upon an automatic device of Collie (*J. Chem. Soc.*, 1889, p. 110), has been constructed by Travers (Dennis, *Gas Analysis*, pp. 209 *et seq.*).

(f) *Absorbents for Nitric Oxide.*

Nitric oxide, NO, is soluble in sulphuric acid of various concentrations. According to Lubarsch (as quoted by Hempel, Gasanal. Methoden*, 4th ed., p. 181), 100 vols. of sulphuric acid ıbsorb:—

	Per cent. H_2SO_4.	Vols. NO.
Monohydrate, H_2SO_4 .	100·0	3·5
$H_2SO_4+2{\cdot}5H_2O$ . .	68·5	1·7
$H_2SO_4+6{\cdot}5H_2O$ . .	45·5	2·0
$H_2SO_4+9H_2O$ . . .	37·7	2·7
$H_2SO_4+17H_2O$ . .	24·3	4·5
Pure water . . .	0·0	7·2

The ordinary absorbent for nitric oxide is a solution of part crystallised ferrous sulphate in 2 parts water, which bsorbs 3 vols. NO. A saturated solution of ferrous chloride vhich must be slightly acidified, to prevent frothing) absorbs wenty-two times its volume of NO; carbon dioxide is equally oluble therein, and must therefore be previously removed by austic alkali. In these solutions the NO is very loosely bound nd partially removed by shaking.

Knorre (*Chem. Ind.*, p. 534) absorbs NO by a saturated olution of potassium bichromate, to which one-fifth of its olume of concentrated sulphuric acid has been added.

This is preferable to potassium permanganate, which has een used for the same purpose.

(g) *Hydrogen*

n be absorbed by finely divided palladium, according to raham (*Chem. Centr.*, 1869, p. 719) and Hempel (*Ber.*, 1879, . 636 and 1006). Generally hydrogen is estimated by comustion with oxygen (or air), as we shall see below; but empel employs Graham's reaction for analysing mixtures of drogen and methane, by first absorbing the hydrogen by lladium sponge, and then burning the methane by explosion; d he has worked out the conditions for performing these erations quantitatively.

Pure palladium is indifferent towards a mixture of hydrogen, ethane, and nitrogen, but if it contains a small proportion of lladious oxide, a partial combustion of hydrogen takes place, d the heat thus generated is sufficient to ensure the absorption of the rest of the hydrogen present; the process is accordingly partly a combustion and partly an occlusion of hydrogen.

The palladium is prepared by heating 4 or 5 g. palladium sponge, in portions of 1 g. at a time, on the lid of a platinum crucible, until it nearly glows, and then allowing it to cool slowly, whereby a thin film of oxide is formed upon the surface of the metal. For use, 4 g. of this oxidised sponge is placed in a U-tube of 4 mm. internal diameter and 20 cm. long; the tube is placed in a beaker, as shown in Fig. 66, and kept at a temperature of 90° to 100° by hot water. To carry out a determination, the U-tube is attached on one side to the burette, and on the other to a pipette charged with water, and the gas syphoned backwards and forwards three times; the beaker H is then replaced by a beaker containing cold water, and the gas again passed twice through the tube, so as to cool it to the original temperature. The volume is finally adjusted by syphoning the liquid in the pipette up to *i*, and the reading is taken; the decrease in volume represents the absorbed hydrogen and the volume of oxygen originally contained in the U-tube. The latter is determined, once for all, by closing

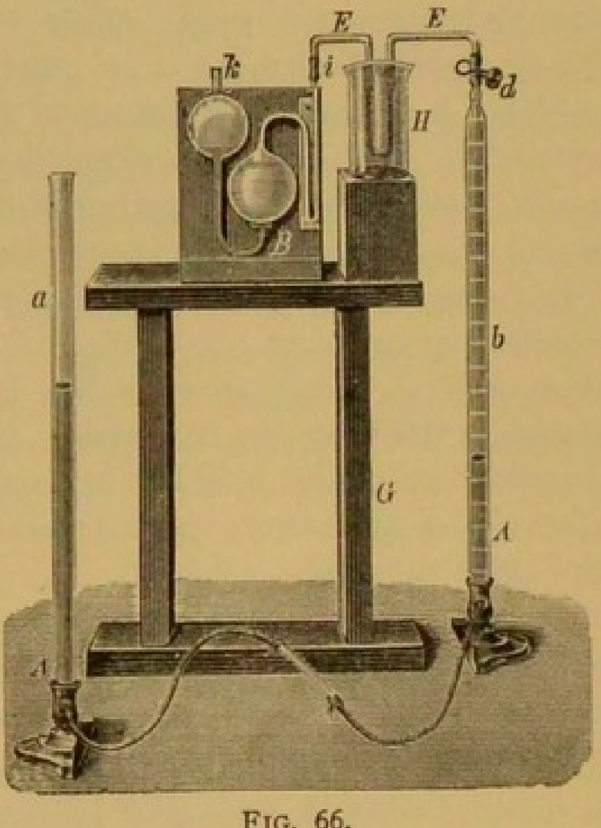


FIG. 66.

one end of the U-tube with a glass stopper attached by a piece of rubber tubing, and then placing it in a beaker of water at 9°; the open end of the tube is then connected with the burette, previously filled with water, and the tube heated in the beaker to 100°. The increase of volume, as measured in the burette, is that due to an increase of 91° in temperature, and therefore equal to one-third of the volume of gas; from this value the volume of oxygen in the U-tube is obtained. The palladium is regenerated after use by first passing air over it, when it gets quite hot; any drops of water that may collect are removed, the palladium is then shaken out of the tube and superficially oxidised as before by heating on the lid of a platinum crucible.

Carbon dioxide and monoxide, oxygen, heavy hydrocarbons, and vapours of hydrochloric acid and of ammonia, prevent the determination of hydrogen by this method, and it is but rarely used in technical gas-analysis. It has, however, the advantage that since no air is added, there is no restriction as to the volume of gas to be used for the analysis.

Palladium hydrosol (sold in a solution of 61 to 63 per cent. by Kalle & Co., Biebrich on Rhine, by the name of *Palladiumsol*), according to Paal and Gerun (*Ber.*, 1908, p. 808), absorbs up o 3000 times its volume of hydrogen. Paal and Hartmann (*Ber.*, 1910, p. 243) employ a solution of 2·44 g. palladiumsol with 2·74 g. sodium picrate (which acts as an oxidiser) in 330 c.c. water. The liquid is kept in one of the Hempel pipettes, and if not in use must be protected against light and air. The absorption of the hydrogen takes place within ten minutes without requiring any shaking, but previously all other absorbable gases, also carbon monoxide, should be removed.

Brunck (*Chem. Zeit.*, 1910, pp. 1313 and 1331) employs for absorbing hydrogen a solution of 2 g. *colloidal platinum* ·5 g. picric acid, neutralised by 22 c.c. normal caustic soda solution, diluted with water to 100 to 110 c.c. The firm of Kalle & Co., at Biebrich, supply the mixture in such a shape that it needs only to be dissolved in 100 c.c. of water, at the price of 10s. per gramme. This solution absorbs theoretically 369 c.c. hydrogen of 0° and 760 mm. pressure. The absorption, promoted by frequent shaking, takes ten to thirty minutes. By this method it is possible to estimate hydrogen in the presence of saturated hydrocarbons.

(h) *Absorbents for Unsaturated Hydrocarbons.*

Lebeau and Damiens (*Comptes rend.*, 1913, clvi. pp. 557 *et seq.*) use as absorbing agent for *acetylene* and its homologue a solution containing 25 g. of mercuric iodide and 30 g. of potassium iodide in 100 c.c. of water, with addition of a fragment of caustic potash. This reagent absorbs 20 times its volume of acetylene, forming a white precipitate. *Olefines* are only dissolved by this reagent to the same extent as by pure water. For the absorption of olefines, sulphuric acid is used, the absorption being made much more rapid by dissolving 1 g. of vanadic anhydride, or 6 g. of uranyl sulphate, in 100 g. sulphuric acid sp. gr. 1·84.

Acetylene is also absorbed by an *ammoniacal solution of cuprous chloride*, by which a reddish brown precipitate of Cu_2C_2 is formed, which is filtered off, washed with dilute ammonia till this runs off colourless, collected in a Gooch crucible, and dried over calcium chloride at 100° in a current of carbon dioxide. Dry copper acetylide may explode already at 60°. This risk is avoided by not drying the moist Cu_2C_2, but determining the copper contained in it (Scheiber, *Berl. Ber.*, 1908, p. 3816).

Acetylene can be also determined by absorbing it in *fuming sulphuric* acid by means of a Hempel pipette.

B.—ESTIMATION OF GASES BY TITRATION.

General Remarks.

Sometimes one (or several) of the constituents of a gaseous mixture is estimated not as described in the last chapter, by the contraction of volume of the gas ensuing on the removal of that constituent by an absorbent, but by chemical examination of the latter. This may be done in various ways; in this section we treat of the estimation by titration, which in the nature of things can take place only in the case of constituents endowed with sufficiently great chemical affinities, and is then carried out wherever possible, especially for technical purposes.

For this purpose the ordinary standard solutions, as generally used in volumetric analysis, may be employed. In many cases, owever, it is preferable to prepare *special standard solutions*, ot indicating the weight but the *volume* of the gas in question. “normal solution” is then that of which 1 c.c. corresponds o exactly 1 c.c. of the gas to be absorbed, assumed to be in he normal state, *i.e.*, at a pressure of 760 mm. of mercury, at temperature of 0°, and absolutely dry. A decinormal solution s one of which 1 c.c. corresponds to 0·1 c.c. of the gas. Someimes, as in ordinary volumetric analysis, viz., where a gas is ot estimated directly, but by retitration, two standard liquids re required. The relation between these must be exactly nown; and in some cases it is not possible to employ normal” solutions, but solutions of which the chemical effect f which is empirically determined.

The titration of the constituents sought for may either take lace while measuring the total volume of the gaseous mixture, r the non-absorbable residue of gas may be measured, which emains after passing the gas through an apparatus containing known volume of titrated absorbing liquid, in which case the um of the amount calculated from the titration and that neasured directly corresponds to the total volume of gas mployed.

In the first case, that where the total volume of the gas is irectly measured, we must distinguish between such estimations or which only a comparatively small quantity of gas is mployed, and such where a large quantity of gas has to e continually examined. In the latter case, the gas to be ested is passed through a gas-meter in which the quantity assing through is recorded; on going out of the meter the as is made to traverse a vessel charged with a measured uantity of absorbing liquid, which after certain intervals, when sufficient quantity of gas has passed through, is retitrated.

Where only a limited quantity of gas is at disposal, it is neasured in a flask of known capacity up to a mark in its neck, which the rubber cork closing the neck is pressed down. his cork has two perforations, one for the tube for passing the as into the flask, the other for the delivery tube of the pipette burette used in titration, as shown in Fig. 67, p. 134. After ling the flask with the gas, the tube through which this has een effected is closed with a glass rod, which is taken out for a oment in order to remove the excess pressure after running a liquid into the flask. In order to estimate the constituent in question, a certain volume of a titrated liquid is run by means of a pipette or burette into the flask, which of course causes the same volume of gas to escape on opening the other tube for a moment, this volume being deducted on calculation of the result from the total contents of the flask. After agitating the flask, the excess of the absorbent is estimated by retitration.

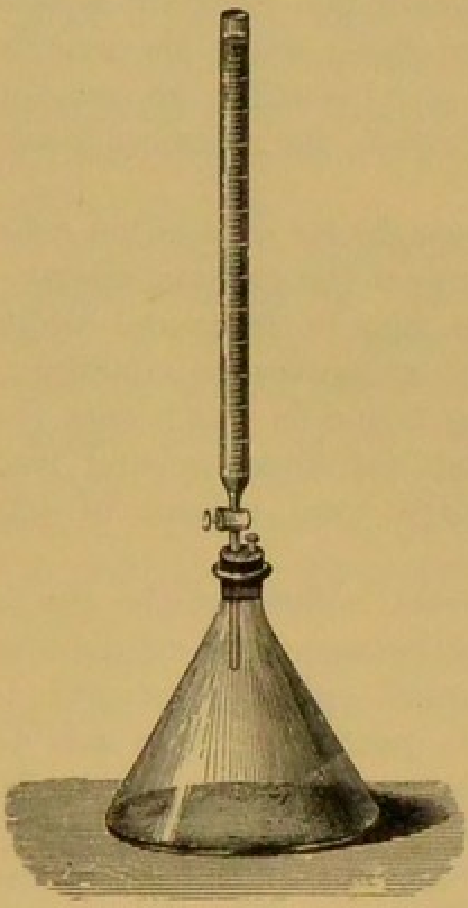


FIG. 67.

In the second class of titration methods, either a measured excess of absorbent is employed, which is afterwards retitrated, or else the gas is passed through a limited quantity of the absorbent until a visible reaction, *e.g.*, a change of colour, proves that the active constituent of the absorbing liquid has been just saturated. The volume of the unabsorbed part of the gas is found by a measuring apparatus attached to the absorbing vessel, which is either connected with an aspirating arrangement, or acts itself as such. Such measuring apparatus, according to the quantity of gas and to the desired degree of accuracy, may be either an ordinary gas-meter, or a water aspirator, or an india-rubber pump which at each stroke aspirates approximately equal volumes of gas. If the estimation of the constituent to be determined is effected by employing an excess of the absorbing liquid and retitration the experiment may be continued until the unabsorbable portion of the gas has reached a certain volume, to be measured either by an automatically shutting-off gas-meter, or by an aspirator from which a definite quantity of water is run off. In that case the non-absorbable portion of the gas is a constant, the absorbable portion a variable magnitude.

It must be borne in mind that the total volume of gas, or that which remains after absorption, is measured under the arying conditions of atmospheric pressure and temperature, hilst the titration of the absorbed gas indicates this in the normal" state (760 mm. and 0° C.). Of course for somewhat xact analysis both volumes must be reduced to the same onditions.

We now enumerate some apparatus constructed for carrying ut the estimation of gases by titration.

1. *Apparatus of Hesse.*—This is represented by the cut, ig. 67, p. 134. It shows a conical bottle of strong white glass,

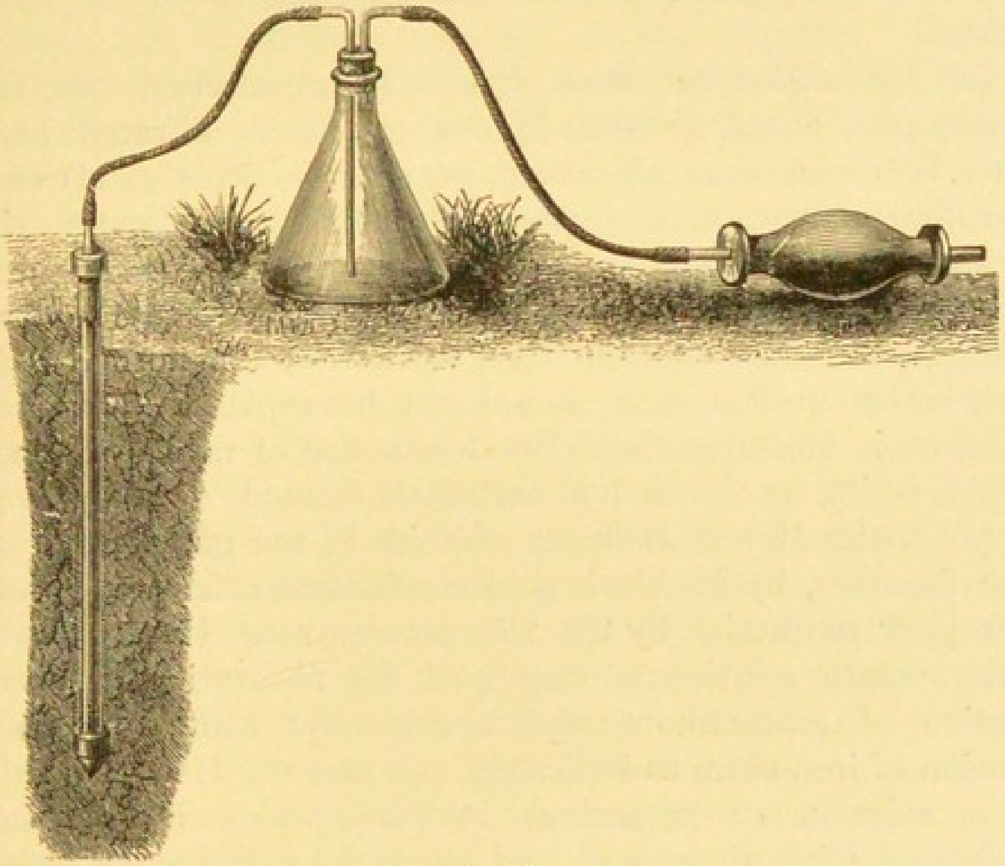


Fig. 68.

olding about 500 or 600 c.c., with a mark in the neck (the contents p to which point are etched on the glass) with a rubber cork, hrough the perforations of which an inlet-pipe and a pipette or urette can be introduced; otherwise they are closed by glass ods. In order to take the sample, the bottle is filled with ater, a portion of which is then displaced by the gas to be xamined, whereupon the cork with its glass stoppers is put in nd pressed down to the mark. If the employment of water ust be avoided, for instance when taking a sample of air ontained in the soil, as shown in Fig. 68, the rubber stoppers provided with an inlet- and outlet-tube is put in the dry bottle, and the gas is drawn into it by means of a rubber pump. When this has been done, the end of the inlet-pipe is drawn out of the stopper, and both openings of this are quickly closed by their glass rods. An excess of a standard solution is now run in, and the volume of gas corresponding to this is deducted from the total. When the action of the absorbent on the gas has been completed by gentle shaking, the cork is taken out and the excess of absorbent is found by retitration.

The following are some of the applications of this apparatus:—

(*a*) Estimation of *carbon dioxide* in atmospheric air, from rooms, pits, caves, subsoil, in coal-gas, etc. Titrated baryta water is employed as absorbent, normal (or decinormal) oxalic acid for retitration, and phenolphthalein as indicator. The baryta water, which is too changeable for being made permanently normal, is employed of an approximately normal strength, and checked from time to time by the normal oxalic acid, which in this case should not be replaced by mineral acids, as it has over them the advantage of not, or but very slowly, acting on the barium carbonate formed.

(*b*) Estimation of *hydrogen chloride* in the gases from salt-cake furnaces, hydrochloric-acid condensers, calcining furnaces for copper extraction by the wet process, etc. Here a normal silver nitrate solution is employed for absorption, a normal solution of ammonium sulphocyanide for retitrating and a solution of iron-alum as indicator. Or else the HCl is absorbed by a solution of potassium hydrate, which is afterwards acidulated with nitric acid and titrated by Volhard's process. Or else a solution of sodium carbonate is employed for absorbing the HCl, retitrating the excess by normal silver nitrate solution, with potassium chromate as indicator.

(*c*) Estimation of *chlorine* in the gases from chlorine stills, from the Deacon process, in the air of bleaching-powder chambers, etc. The absorbent is a normal solution of arsenious acid in sodium bicarbonate, the excess being retitrated by normal iodine solution, with starch solution as indicator.

(*d*) For estimating both *chlorine and hydrogen chloride* a second volume of gas is employed, the absorbent for this being a solution of arsenious acid in sodium carbonate; this is afterwards acidulated with nitric acid, and the total HCl, viz., that originally present *plus* that formed from the chlorine, is titrated as above-mentioned with silver solution and ammonium sulphocyanide. Since each volume of chlorine produces two volumes of HCl, twice the volume of the free chlorine must be deducted from the total volume of HCl.

Both in this case and the last, it is more important to ascertain the *weight* of HCl and Cl than the volume. It is therefore preferable here not to make the calculations by volume, but to employ, in lieu of the "normal" solutions otherwise used in gas-analysis, *i.e.*, such as indicate 1 c.c. of gas per 1 c.c. of the reagent, the "decinormal" solutions of ordinary volumetric analysis, or else solutions indicating 0·001 grain per cubic centimetre, or parts of a grain as the case may be.

(*e*) Estimation of *sulphur dioxide* in the gases of pyrites-kilns, chimneys, glass-houses, etc. The absorption is performed by a solution of sodium carbonate of arbitrary, but not too high strength; a little starch solution is added and the re-titration made by iodine solution.

2. *Apparatus of Reich* (as modified by Lunge), Fig. 69. This belongs to that class of apparatus where the non-absorbed gaseous remainder is measured. The bottle A, holding about a litre, is about half filled with the absorbing liquid through the tube *d*, which is then closed by a rubber cork. Into one of the lateral necks enters a pipe *a*, drawn out to a point and bent at the end, or provided with a number of pinhole outlets, and closed on the outside by the pinchcock *m*. Through the cork of A passes also the outlet *e*, which is connected by *f* with the aspirating bottle B. Tube *g* goes to the bottom of B and on the outside is connected with the rubber tube *h*, with pinchcock *i*. Underneath this a glass jar C is placed, holding half a litre and divided into cubic centimetres.

The absorbing vessel is filled rather more than half, the aspirator B entirely with water; all corks are put in tightly, the pinchcock *m* is closed and the apparatus is tested for tightness by opening tap *i*. The flow of water, which at first is continuous, should soon change into slow dropping and at last cease entirely, if there is no leakage in the apparatus.

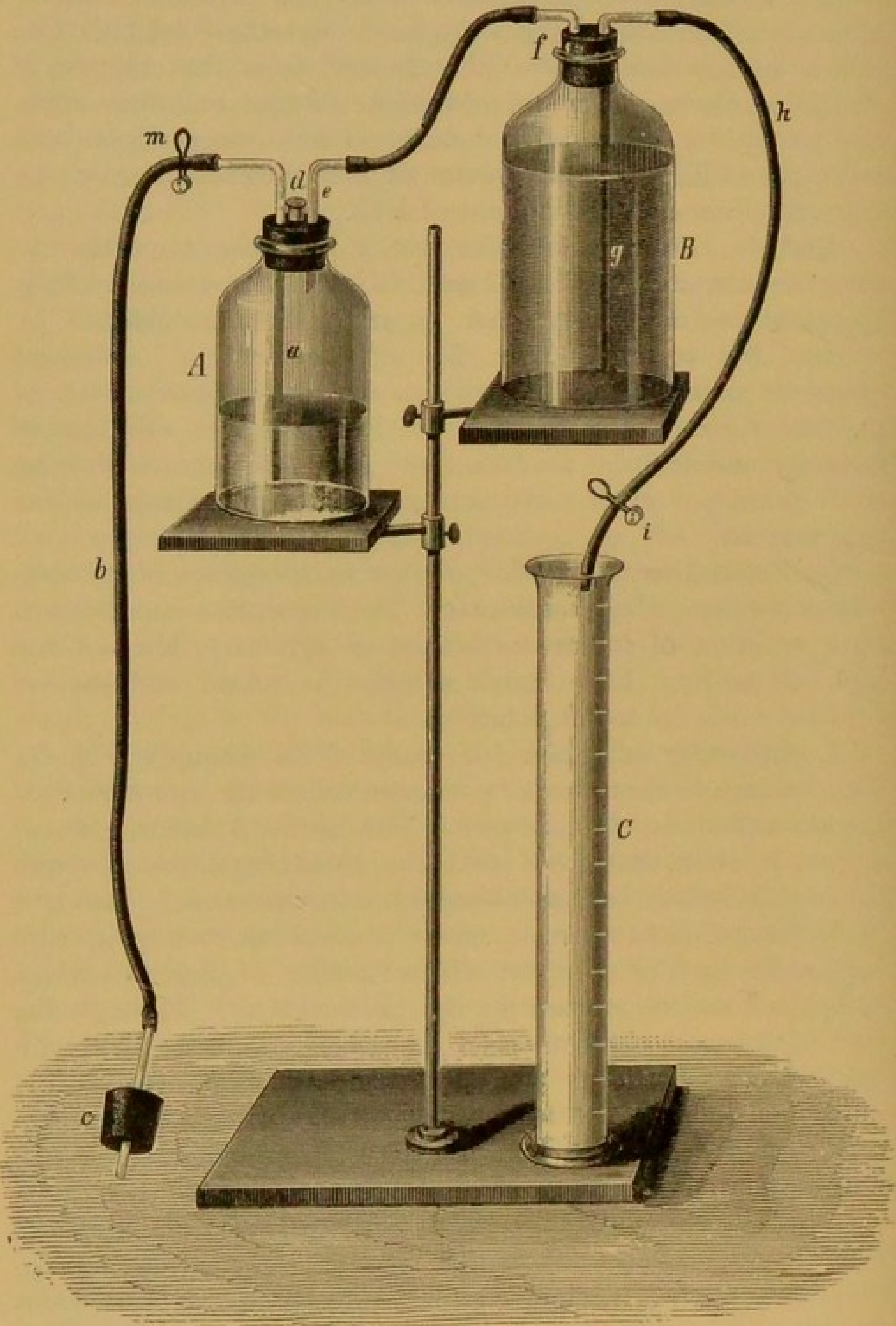


FIG. 69.

A suitable volume of absorbing liquid is now run into A by means of a pipette; if necessary, also an indicator, and the central neck is again tightly closed.

The inlet-pipe is now filled up to the pinchcock m by means of a small india-rubber pump, and water is run off through tap i until the liquid in the inlet-pipe has just been forced down to its point, or until a single bubble of gas has come out, in order to bring the air contained in A to the same pressure as that prevailing during the test. The jar C is emptied and again put under the aspirator.

Now the inlet-pipe b is connected with the source of the gas to be tested, pinchcock m is opened entirely, and after this tap i so far that the gas is just drawn into A. It is thus passed through A in a slow stream, shaking this bottle from time to time, until the indicator shows that the absorbent is saturated with the constituent to be determined. At this moment both taps are closed, and the test is complete. Of course another test may follow immediately, after adding a fresh quantity of absorbent. The bottle A needs only after a series of tests emptying, cleaning, and refilling.

The volume of water run into C at each test is that of the residual gas; that of the absorbed gas follows from the quantity and strength of the absorbing-solution employed. The calculation is made as follows:—If we call the volume of the employed normal solution n c.c., that of water run out during the test m c.c., there would be, apart from all the corrections:

n = the volume of the gaseous constituent absorbed;
m = the unabsorbed residue of gas;
$n+m$ = the total volume of gas employed in the test.

The percentage (by volume) of the constituent found by titration to the total volume of the gas tested is:

$$\frac{100n}{n+m}.$$

For accurate estimations we have to consider that n means a corrected, m an uncorrected volume of gas. Hence, in order to get an accurate result, m must be corrected in the manner explained *suprà*, pp. 17 *et seq.*, or by the mechanical apparatus described p. 19.

This proceeding will be made clearer by describing in detail the operation for which Reich's apparatus was intended in the first place, viz., *the estimation of sulphur dioxide in pyrites-kiln gases.* Add a little clear starch solution to the water contained in the absorbing bottle A; by means of a pipette put in a suitable quantity of decinormal iodine solution, say 10 c.c., and draw the gas to be tested through the liquid until the blue colour has been almost, but not entirely, destroyed. It is not advisable to go up the entire decolorisation of the liquid, because thereby the experiment is very easily overdone; should this have happened, the liquid must be coloured faintly blue by adding one or more drops of iodine solution before commencing a new test. When testing gases containing but little SO_2, it is advisable to add a little sodium carbonate to the absorbing liquid; but in this case bottle A must be freshly charged each time, because otherwise CO_2 would be given off and would cause an error by increasing the volume of the unabsorbed gas.

The calculation is made as follows:—Since the reaction is: $2I+SO_2+2H_2O=2IH+SO_4H_2$, the 10 c.c. decinormal iodine solution (=0·12692 g. I) correspond to 0·032035 g. SO_2. This is=10·95 c.c. SO_2 at 0° and 760 mm. Suppose that 128 c.c. water has run out, this is equal to the same volume of gas not absorbed by iodine solution. Hence there was present:

$$\frac{10{\cdot}95 \times 100}{138{\cdot}95} = 7{\cdot}88 \text{ volume per cent. } SO_2.$$

The following table makes this calculation unnecessary:—

c.c. of water run out.	Vol. per cent. SO_2 in the gas.	c.c. of water run out.	Vol. per cent. SO_2 in the gas.
80·3	12·0	126·0	8·0
84·3	11·5	135·1	7·5
88·6	11·0	145·5	7·0
93·4	10·5	157·6	6·5
98·6	10·0	171·6	6·0
104·4	9·5	188·2	5·5
110·8	9·0	208·1	5·0
117·9	8·5		

N.B.—When using this table, the 10·95 c.c. corresponding to the iodine consumed must *not* be added to the volume of the water run out.

In the calculation as described, no regard is taken of temperature and barometric pressure. If this is to be done, the volume read off must be reduced to 0° and 760 mm. as above mentioned. If this correction is neglected, considerable errors, of 10 per cent. and upwards, will be caused in this calculation if the test is taken at somewhat high temperatures and low barometric pressures.

Reich's method has been applied by Lunge (*Z. angew. Chem.*, 1890, 563) to the *estimation of total acids in pyrites-kiln gases and analogous gases.* Since these gases always contain some, and may contain a considerable proportion of *sulphur trioxide* which is not indicated by the iodometrical estimation, it is preferable to express the value of such gases by their percentage of *total acids*, *i.e.* SO_2+SO_3. In such cases the best absorbent is a standard solution of potassium or sodium hydroxide, of which a suitable quantity is put into the bottle A, Fig. 69 (or into the bottles specially employed for this purpose by Lunge and others, which will be described later on). The indicator in this case is an alcoholic solution of phenolphthalein (1 : 1000), of which a few drops are added, sufficient to give to the liquid a vivid red colour. The gas is not drawn through it continuously, but in small portions at a time, agitating each time about half a minute. Any arsenious acid carried along by the gas is kept out by interposing a small glass tube filled with asbestos. The operation is finished when the last pink shade has vanished, which is easily noticed even in the dusk or when employing artificial light by employing a white paper as background. At this point normal sulphite and sulphate (Na_2SO_3 and Na_2SO_4) are formed. Other indicators, *e.g.* litmus, are not admissible, as they yield different results for sulphurous and sulphuric acid.

If HCl is present as well, it can be estimated in the liquid, after titrating for total acids as just described, by Volhard's method (titration with silver nitrate and retitrating with ammonium sulphocyanide).

The Reich apparatus is employed by Raschig (*Z. angew. Chem.*, 1909, xxii. p. 1182) for estimating in vitriol-chamber gases both sulphur dioxide and nitrous gases, by charging it with 10 c.c. of decinormal iodine solution, about 100 c.c. water, a little starch solution, and 10 c.c. of a cold saturated solution of sodium acetate. The chamber gases are passed through, taking care that no droplets of sulphuric acid get into the iodine solution, which is prevented by a glass-wool filter. The calculation of the *sulphur dioxide* is carried out as stated *suprà*, p. 110. In order to estimate the *nitrous gases*, a drop of phenolphthalein is now added to the decolorised liquid and decinormal caustic soda solution is added until a pink colour appears. From the number of cubic centimetres of soda solution required for this, 10 c.c. is deducted for HI and 10 c.c. for the sulphuric acid formed by the reaction:

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI.$$

The decinormal soda solution required in excess of these 20 c.c. indicates the nitric or nitrous acid present.

The same apparatus can be used for estimating the *sulphur trioxide* formed by the passage of burner-gases through contact apparatus. The catalysed gases are passed through a measured quantity of iodine solution, where the SO_2 is oxidised to H_2SO_4. The iodine left in the free state is determined by thiosulphate solution, and the total acidity by baryta or decinormal soda solution and phenolphthalein, making the same deduction of acid as in the Reich-Raschig method (p. 110). If the cubic centimetres of decinormal iodine solution consumed are called a, and those of decinormal soda (or baryta) $= b$, the quantity of uncatalysed SO_2 is: $x = 0{\cdot}0032\,a$ g. and that of SO_3 formed: $y = 0{\cdot}004\,(b - 2a)$. The yield of SO_3 in per cent. by volume is:

$$\frac{(b - 2a)100}{b - a}.$$

A modification of the Reich apparatus, constructed by Rabe, is sold by H. Göckel, Berlin N.W. 6.

3. *The Minimetric Method.*—This method was in the first instance indicated by R. Angus Smith, who applied it to the approximate estimation of *carbon dioxide in air*, by producing, as final reaction, a certain just visible degree of turbidity in the absorbing liquid, which consisted in a solution of lime or baryta in water. I myself also employed this method (Lunge, *Zur Frage der Ventilation*, 1877), but I soon rejected it in its original shape, because the final reaction is too uncertain, and varies too much according to the degree of light in the locality. I therefore worked out another method based on titration, with the assistance of Zeckendorf (*Z. angew. Chem.*, 1888, pp. 395 *et seq.*), which will now be described. Fig. 70 shows the apparatus employed. The bottle A (which may also have a conical shape) holds about 150 c.c. (the exact contents being marked on it) and

receives a measured quantity of the absorbent to be employed. Through its doubly perforated rubber cork, which reaches down to a mark in the neck of A, passes an inlet-pipe, ending just below the cork, and an outlet-pipe, connected by strong rubber tubing with the india-rubber ball or "finger-pump" B. This pear-shaped ball is provided with clack-valves, and at each compression by the hand of the operator delivers about 70 c.c.; the quantity to be ascertained by a number of trials.

In making a test, the bottle A is first left empty. Then the bulb B is firmly compressed with the right hand, and allowed to expand again, whereby it is filled with the air of the space to be examined; this is best repeated a few times. Now the bottle A is opened, 110 c.c. of the reagent is quickly run in from a pipette, the cork is at once put on and the air contained in bulb B is slowly pressed in by squeezing the bulb, shaking B with the other hand. This agitation is continued for another minute, taking care that the whole gaseous contents of A come into contact with the liquid. This liquid in testing air for CO_2 consists of a *n*/500 solution of sodium carbonate (here the term "normal" = *n* is understood in the ordinary, not the gas-volumetric sense), coloured red by dissolving 0·02 g. phenolphthalein in a litre of it. The colour of this solution gradually turns paler, as more and more bulb-fillings are forced through and out; in perfectly pure air of woods or fields more than forty bulbsfull would be required for discharging it; in the air of ordinary living-rooms, about nine or ten bulbs; in strongly contaminated air, correspondingly less, down to two or three bulbsfull. The pink colour is destroyed and turned into light yellow, when all the Na_2CO_3 has been converted into $NaHCO_3$, and a trace of free CO_2 is superadded.

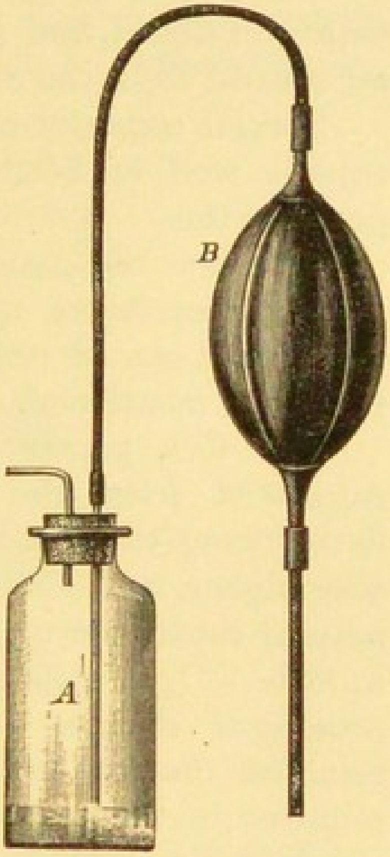


FIG. 70.

The above-mentioned sodium carbonate solution (*n*/500 = 0·0106 g. Na_2CO_3 per litre) must not be kept for any length of time in half-filled or not tightly closed vessels, as it is spoilt already in a few hours by the action of the CO_2 in the air of the room. It is therefore preferable to keep only a decinormal solution (= 5·3 g. Na_2CO_3 per litre) in stock, which is coloured red by 1 g. phenolphthalein (dissolved in alcohol) per litre. Before actual use, 2 c.c. of this *n*/10 solution is diluted with distilled, freshly boiled (and cooled) water to 100 c.c., and of this *n*/500 solution, which must have still a strongly red colour, 10 c.c. is used for each test. In between the 100 c.c. flask is kept well closed, and if the experiments have to be interrupted for several days, the dilute solution is thrown away.

Special experiments showed that the *n*/10 solution keeps equally well in bottles of ordinary glass and in Bohemian potash glass.

Of course the quantity of air originally present in the bottle A also contributes to the result, but as this magnitude is constant, it can be neglected in drawing up the empirical table to be just mentioned.

The CO_2 present in the air tested cannot be simply calculated from the number of bulb-fillings required for decolorising the 10 c.c. of *n*/500 solution; it is always considerably higher, and all the more so the purer the air. Various reasons contribute to this result, more particularly the fact that a little CO_2 is expelled from the Na_2CO_3 solution by mere prolonged shaking with air free from CO_2. In order to establish the real relation between the number of bulb-fillings required in the test, and the actual percentage of CO_2 in the air, Lunge and Zeckendorf made a prolonged series of experiments with all possible precautions, which led them to draw up the following table:—

Number of bulb-fillings.	CO_2 in air. Per cent. by vol.	Number of bulb-fillings.	CO_2 in air. Per cent. by vol.	Number of bulb-fillings.	CO_2 in air. Per cent. by vol.
2	0·300	11	0·087	20	0·062
3	0·250	12	0·083	22	0·058
4	0·210	13	0·080	24	0·054
5	0·180	14	0·077	26	0·051
6	0·155	15	0·074	28	0·049
7	0·135	16	0·071	30	0·048
8	0·115	17	0·069	35	0·042
9	0·100	18	0·066	40	0·038
10	0·090	19	0·064		

Fuchs (quoted by Lehmann, *Prakt. Hygiene*, 1900, p. 149) has found these empirically established results to be correct, but he prefers employing a solution of twice the strength, *i.e.*, 4 c.c. of the *n*/10 solution diluted to 100 c.c. His results agree to about one-tenth of their value.

This apparatus can be also used for estimating the small quantities of *hydrogen chloride* in the air of alkali works, etc., employing a decinormal solution of potassium hydrate as absorbent, with methyl orange as indicator; or the *total acids* in acid-smoke, etc., with potash solution and methyl orange (as described p. 141), or the sulphur dioxide in chimney-gases, etc., with iodine solution and starch.

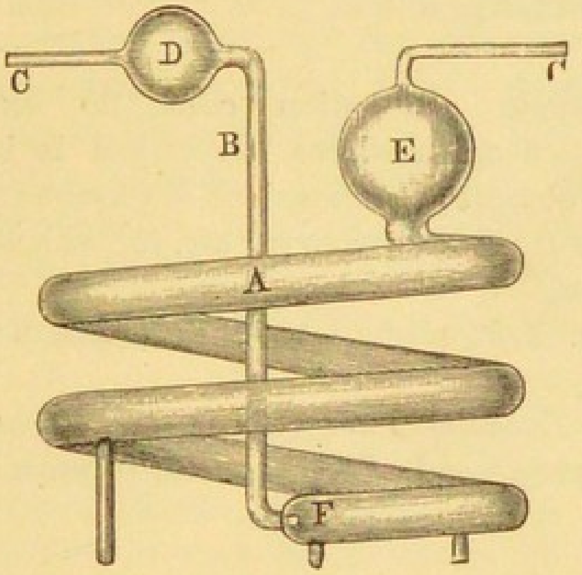


FIG. 71.

4. *Various Apparatus for estimating Gaseous Constituents occurring in Minute Quantities.*—In these, as in the preceding cases, the gas should be brought into intimate contact with the absorbent, frequently during a certain length of time. Of the numerous apparatus constructed for this purpose we describe the following:—

1. *Winkler's Absorption Coil* (Fig. 71) consists of a spiral glass tube A, resting on three glass feet, and filled with the absorbing liquid nearly up to the bulb E. Into its bottom is sealed the inlet-tube B, provided with a bulb D and a pointed end F. From the latter the gas entering at C issues in small bubbles, like a string of beads travelling upwards singly in the coil A, and leaving it after a comparatively long time at C_1.

The gradient of the wall must be gentle and quite uniform; otherwise the small bubbles unite into large ones, which should be avoided, because there is then too little contact between the gas and the liquids. Many of the coils found in trade do *not* fulfil this requirement; we therefore quote suitable dimensions for two different sizes of coils (in millimetres):—

	Size 1.	Size 2.
Width of A	22·0	7·5
„ B	10·0	4·5
„ C and C_1	6·5	4·5
Diameter of bulb D	35·0	15·0
„ E	60·0	30·0
Diameter of coil A	200·0	80·0
Height from foot to bulb E	170·0	80·0

Properly made absorption coils do excellent service, especially in such cases where the object is less the estimation than the complete removal of a gaseous constituent, *e.g.* carbon dioxide from atmospheric air, for which purpose size 1 is most suitable.

Kyll (*Chem. Zeit.*, 1896, p. 1006) describes a modification of this apparatus.

2. *Lunge's Ten-bulb Tube* (*Z. angew. Chem.*, 1890, p. 567), Fig. 72, has a very good effect, superior to most other apparatus of this kind, when the constituent in question is to be estimated either volumetrically or gravimetrically, because the gas-bubbles are constantly broken up again. The large bulb in the entrance tube prevents the liquid from being forced back by atmospheric pressure.

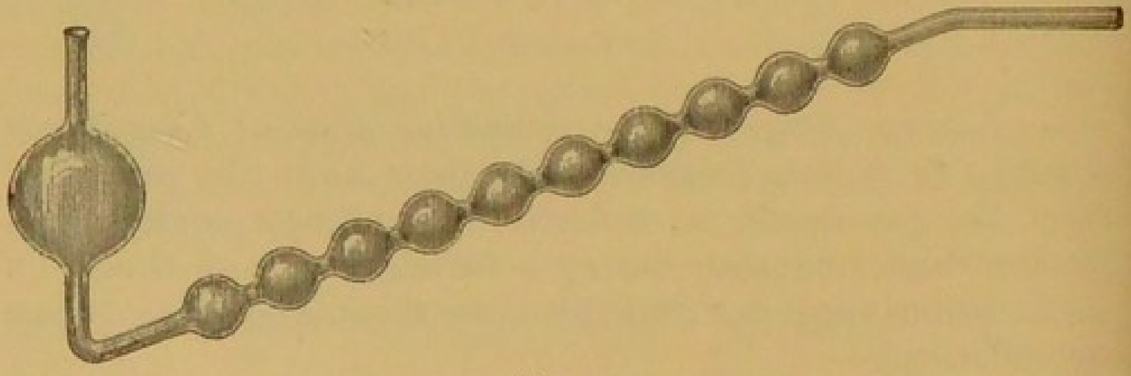


FIG. 72.

3. *Volhard's Absorbing Flask*, Fig. 73 (Volhard, *Ann. Chem.*, clxxvi. p. 282), improved by Fresenius (*Z. anal. Chem.*, 1875, p. 332) by the addition of another bulb in the lateral tube. They are mostly made about 11 cm. high, 7 cm. wide at the bottom, and 2·5 cm. wide at the top, and are charged with from 25 to 50 c.c. of liquid, which by the pressure of the gas is partially forced up into the lateral tube. After finishing the absorption, the liquid can be titrated in the flask itself.

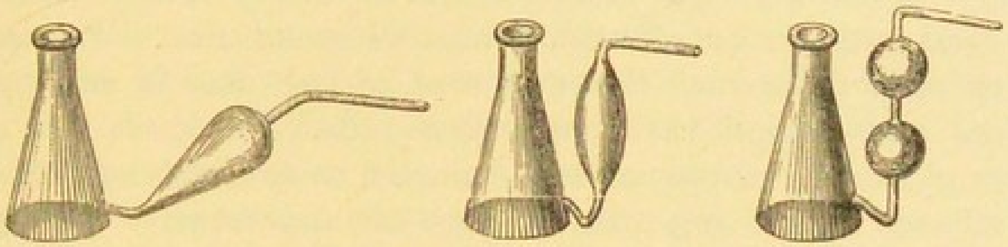


FIG. 73.

4. *Drehschmidt's Absorbing Cylinder*, Fig. 74.—The central tube, passing through the rubber cork, ends at the bottom in a closed glass bulb, with pin holes in the upper part, by which the gas is divided into very small bubbles.

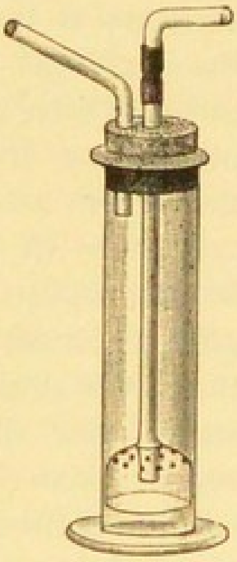


FIG. 74.

C.—ESTIMATION OF GASES BY WEIGHT.

The estimation of gases by weight is exceptionally performed in such cases where the constituent in question is only present in very slight quantity, and where we possess no convenient volumetric methods for the purpose.

The gases are for this purpose passed through absorbing apparatus of the same kind as those described *suprà* for the estimation by titration, pp. 132 *et seq.*, and the calculation of the results is made in the way as described there.

We here mention some applications of this method.

1. *Estimation of Hydrogen Sulphide, Carbon Disulphide, and Acetylene in Coal-gas.*—The gas, before entering the meter or the aspirator where it is to be measured, passes through two Volhard's absorbing flasks, *vide suprà*, each of them containing 25 c.c. of a concentrated ammoniacal solution of silver nitrate, then through a combustion tube of about 25 cm. length, filled

with platinised asbestos (the preparation of which will be described later on, and heated to an incipient dark red heat; finally again through two Volhard's flasks, each of them charged with 20 c.c. of ammoniacal silver solution. To make quite sure, three such flasks instead of two may be employed before and behind the combustion tube. For each test 100 litres of gas are employed, and from ten to twelve hours should be allowed for passing them through the apparatus.

The contents of the receivers placed in front of the combustion tube after some time show a whitish, then a darker turbidity, caused by the precipitation of the silver compounds of hydrogen sulphide and acetylene which are absorbed there.

The carbon disulphide and other sulphur compounds present in coal-gas, on passing through the combustion tube and coming in contact with the hot platinised asbestos, form hydrogen sulphide, which is absorbed in the following receivers, and causes there a blackish brown precipitate of silver sulphide.

After finishing the operation, the contents of the receivers in front of the combustion tube are united, and also those of the receivers behind the tube. They are separately passed through filters, and the precipitates are carefully washed. The precipitate from the front receivers is cautiously covered on the filter with dilute hydrochloric acid, keeping the funnel covered with a watch-glass. This causes the silver acetylide to decompose into gaseous acetylene, which escapes with slight effervescence, and silver chloride, which remains mixed with the silver sulphide. After washing the mass on the filter with water, the silver chloride is extracted by dilute ammonia, reprecipitated from the filtrate by saturating this with nitric acid, and then dried and weighed in the usual manner. From the weight of this silver chloride that of the *acetylene* originally present in the coal-gas can be deduced by means of the following formula (founded on the research of E. K. Keiser, *Amer. Chem. J.*, xiv. p. 285):

$$C_2Ag_2 + 2HCl = 2AgCl + C_2H_2.$$

That means that 1 g. AgCl corresponds to 0·09072 g. acetylene =84·03 c.c. at 760 mm. and 15° C. in the moist state.

On the filter, after extracting the silver chloride, only silver sulphide remains, corresponding to the *hydrogen sulphide* originally present in the coal-gas. After burning the filter, the Ag_2S can be immediately converted into metallic silver by heating it in a current of hydrogen. One g. of silver found in this way corresponds to 0·1486 g. S, or 0·1579 g. H_2S, or 103·78 c.c. H_2S of 760 mm. pressure and 0° C. in the original gas.

The silver sulphide precipitated in the receivers placed behind the combustion tube has been produced from the other sulphur compounds present in coal-gas, such as *carbon disulphide*, *phenyl sulphocyanide*, etc. It is equally converted by the just-described process into metallic silver, which is weighed and calculated as *carbon disulphide*, since this compound is always predominant. One g. of silver = 0·1486 g. S corresponds to 0·1764 g. $C'S_2$, or 52·12 c.c. of vapour of CS_2 at 760 mm. pressure and 0° C.

It is not usual to express the percentage of H_2S and CS_2 in coal-gas by volumes, or by weight, but generally only the number of grammes of sulphur contained in 100 cb.m. (in England grains per cubic foot; 1 g. per cubic metre = 0·4372 gr. per cubic foot) is indicated as the *total sulphur* contained in the gas. This is generally estimated by burning a known volume of the gas and receiving the products of combustion in a solution of potassium carbonate containing a little bromine, from which solution the sulphuric acid formed is precipitated by barium chloride. One g. $BaSO_4$ = 0·1373 g. S. Special apparatus for this purpose have been described by Drehschmidt (*Chem. Zeit.*, 1887, p. 1382) and by F. Fischer (*Z. angew. Chem.*, 1897, p. 302). Since those gases occur in coal-gas merely in minute quantities, their volumes need not be counted when calculating the results, the unabsorbed gas measured in the meter or aspirator being assumed as equal to the total volume of gas tested.

The calculation of the results will be made clearer by giving an example of a special case.

State of barometer, 733 mm.; thermometer, 18° C.
Volume of gas employed, 107 litres.
Corrected for 760 mm. and 0°, 94·787 litres.
Found by weighing:

AgCl = 0·3190 g. = 24·92 c.c. acetylene.
Ag*a* = 0·0111 „ = 1·15 „ hydrogen sulphide.
Ag*b* = 0·3888 „ = 20·26 „ carbon disulphide.

Total sulphur:

$$\begin{array}{lll} \text{Ag}a = 0{\cdot}0111 \text{ g.} & = & 0{\cdot}001647 \text{ g. S} \\ \text{Ag}b = 0{\cdot}3888 \text{ ,,} & = & \underline{0{\cdot}057765} \text{ g. S} \\ & & 0{\cdot}059412 \end{array}$$

100 cb.m. of gas contain 62·68 g. sulphur.

Expressed in per cent. by volume:

Acetylene . . .	0·02629 per cent.
Hydrogen sulphide . .	0·00121 ,,
Carbon disulphide . .	0·02126 ,,

2. *Estimation of Sulphuretted and Phosphoretted Hydrogen in Crude Acetylene.*—The sulphur in technical acetylene gas exists mostly in the shape of organic sulphur compounds, which have been separated from it by Knorre and Arendt (*Verh. Gewerbfleiss*, 1900, p. 155). It is, however, admissible to express them in terms of H_2S, or else in grammes S per cubic metre.

Lunge and Cedercreutz (*Z. angew. Chem.*, 1897, p. 651) have described the following process for estimating both these impurities at the same time:—A known volume of gas is slowly passed through a ten-bulb tube (p. 146), charged with a 2 or 3 per cent. solution of sodium hypochlorite. The liquid is washed into a graduated flask, and in one half of it the sulphuric acid is gravimetrically estimated as barium sulphate (1 g. $BaSO_4$=0·1373 g. S=0·1459 g. H_2S=95·86 c.c. H_2S); in the other half the phosphoric acid is estimated as magnesium pyrophosphate (1 g. $Mg_2P_2O_7$=0·2784 g. P=0·3055 g. H_3P= 200·91 c.c. H_3P).

Dennis and O'Brien (*J. Ind. and Eng. Chem.*, 1912, No. 11, Nov.) propose to improve this method, first, by evolving the acetylene from the calcium carbide without marked rise of temperature in a small Kipp apparatus by means of a saturated solution of sodium chloride; secondly, by employing as absorption apparatus a Friedrichs gas-washing bottle, modified so that the apparatus can be easily rinsed out with water at the close.

3. *Detection and Approximate Estimation of Very Small Quantities of Sulphur Dioxide and Sulphuric Acid in Air, suspected of being contaminated by Acid-smoke.*—Ost (*Chem. Zeit.*, 1896, p. 170) and H. Wislicenus (*Z. angew. Chem.*, 1901, p. 689) chemically fix the acid contained in the suspected air of

forests, etc., by exposing to it during a long time wooden frames, of a superficial area of 1 sq. m., covered with loose cotton tissue, impregnated with barium carbonate by moistening with baryta water. This gives an idea of the quantity of *soot* present, and later on by incineration and estimation of the sulphate contained in the ash shows the quantity of the *acids of sulphur* present in the air.

For the conclusions to be drawn from this process (which is not yet fully worked out) we must refer to the originals.

Cf. also the description in Lunge-Keane's *Techn. Methods*, .. pp. 384 *et seq.*

III. ESTIMATION OF GASES BY COMBUSTION.

General Observations.

A number of gases, especially of those which cannot be estimated by physical or chemical absorption, can be transformed by combustion with oxygen into compounds which admit of determination, either by the contraction of volume caused by their condensation to the liquid state, or by absorption by chemical reagents. The former takes place by the formation of water from hydrogen or compounds containing this in chemical combination, the latter principally by the formation of carbon dioxide.

The oxygen required for combustion is sometimes already contained in the gaseous mixture to be analysed. If not, it is in technical analysis usually added in the shape of atmospheric air, only exceptionally in that of pure oxygen, and in both cases in reasonable excess of that which is required for complete combustion. A suitable mixture having been prepared, the combustion is effected either suddenly by explosion, or slowly by passing the mixture over a heated number of the platinum group. Hereby the hydrogen, both that present in the free state and that existing in the shape of hydrocarbons, is transformed into water, which on cooling separates in the liquid state; the carbon is transformed into carbon dioxide, which is estimated by absorption with caustic alkali in the usual manner.

Changes of Volume by the Combustion and Calculation of the

Single Combustible Gases.[1]—We need here consider only three gases: hydrogen, methane, and carbon monoxide. The other combustible gases, all of them hydrogen compounds, are more suitably previously taken out by absorption, as described on pp. 117 *et seq.* Usually this is also done with carbon monoxide (*cf.* pp. 126 *et seq.*), but sometimes it is more convenient to estimate this by combustion.

The above-mentioned three gases, when burned, produce the following changes of volume :—

Hydrogen.—2 vols. H_2 + 1 vol. O yield water, H_2O, which completely condenses on cooling, thus causing a contraction of the volume, two-thirds of which correspond to the hydrogen originally present.

Methane. — The reaction is: $CH_4+2O_2 = CO_2+2H_2O$. Hence 2 vols. CH_4+4 vols. O = 6 vols. on combustion yield 2 vols. CO_2, the water being removed from the gas in the liquid state. The contraction occurring on combustion is therefore: 6 – 2 vols. = 4 vols., half of which = 2 vols., represents the originally present methane, whose volume is therefore equal to half of the contraction caused by the combustion, or, if the carbon dioxide is removed by absorption, to one-third of the total contraction.

Carbon Monoxide.—2 vols. CO+1 vol. O_2 = 3 vols. of the mixture yield 2 vols. CO_2; hence two-thirds of the contraction represent the carbon monoxide. Or, if we remove the CO_2 by absorption, the carbon monoxide is equal to one-third of the total contraction.

Oxygen can be estimated in a gaseous mixture by adding a measured excess of hydrogen effecting the combustion, and calculating the amount of oxygen from contraction: $O_2+2H_2=2H_2O$, one-third of which is due to the oxygen originally present.

If only one of the combustible gases has to be counted with, we may for methane and carbon monoxide choose to calculate the original volume, either from the contraction after combustion, or from the carbon dioxide formed, or from the total contraction after absorption of the carbon dioxide. The last,

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[1] From the paper of O. Pfeiffer in Lunge and Berl's *Chemische-technische Untersuchung-methoden*, 6th ed. (1911), vol. iii. pp. 242 *et seq.*

which produces the greatest values to be observed, naturally yields the most exact results.

The calculation is more complicated in case of mixtures of two or all three of the combustible gases here considered.

Hydrogen along with Carbon Monoxide.—The hydrogen by itself is equal to two-thirds of the contraction produced by the combustion, since the carbon monoxide on combustion yields its own volume of carbon dioxide. The volume of carbon monoxide originally present is equal to that of the carbon dioxide formed on combustion, and found by the subsequent absorption of this.

We illustrate this by an example of the combustion of a mixture of hydrogen, carbon monoxide, and nitrogen.

Gaseous mixture employed . .	21·1 c.c.
Air added	97·5 „
Together	118·6 c.c. employed.

Volume after combustion . .	102·1 c.c.
Contraction . . .	16·5 „
H	9·53 „
After absorbing the CO_2 . .	97·7 „
CO_2 formed . . .	4·4 „
CO	4·4 „

If *hydrogen, carbon monoxide, and methane* are all present in a gaseous mixture, we must first ascertain the total volume of the combustible gases, $V = H + CO + CH_4$, which in technical gaseous mixtures presupposes ascertaining the quantity of *nitrogen* mixed with those gases. We start from the known percentage of nitrogen, N_1, in the air added for combustion, viz., $N_1 =$ volume of that air $\times$ 0·7905. After accomplishing the combustion, absorbing the CO_2 formed and the excess of atmospheric oxygen, a nitrogen volume $= N_2$ remains, which must be at least equal to N_1. The difference $N_2 - N_1$ shows the amount of nitrogen N present in the gaseous mixture B employed. From this follows:—

(a) *Combustible Gases* $V = R - N$.

(b) *Hydrogen.*—Since, on the other hand, $V = H + CO + CH_4$, we have

$$H = V - (CO + CH_4).$$

Since, moreover, the volume of the total carbon dioxide formed on combustion is equal to that of the carbon monoxide and methane burned: $CO_2 = CO + CH_4$, we may alter the just given equation into—

$$H = V - CO_2,$$

and we thus ascertain the volume of hydrogen present.

(c) *Carbon Monoxide.*—If we add the total contractions (C) we get:—

1. $C = \frac{2}{3}H + \frac{3}{2}CO = 3CH_4$, and from this—

2. $H = \frac{2}{3}C - CO - 2CH_4$. Since moreover (*vide suprà*)—

3. $V = H + CO + CH_4$, and therefore—

3*a*. $CO = V - H - CH_4$, we get by introducing the value of H from equation No. 2.

4. $CO = V - (\frac{2}{3}C - CO - 2CH_4) - CH_4$, or

$$= V - \frac{2}{3}C + CO + CH_4.$$

Now, as we have seen *sub b*, $CO + CH_4 = CO_2$, we ultimately get—

$$CO = V - \frac{2}{3}C + CO_2.$$

(*d*) *Methane.*—According to the above equation, No. 3—

$$CH_4 = V - H - CO.$$

By replacing H by the value stated *suprà* in No. 2, we get—

$$CH_4 = V - (\frac{2}{3}C - CO - 2CH_4) - CO,$$

$$= V - \frac{2}{3}C + 2CH_4,$$

$$= \frac{2}{3}C - V.$$

(An example of this calculation in a special case is given *suprà*, p. 110, when describing Pfeiffer's apparatus.)

If we call—

Vol. I. = Gaseous remainder (R) + air,
" II. = Remainder after explosion,
" III. = " absorbing the CO_2 formed in combustion,
" IV. = " " oxygen in excess,

we find therefrom :—

C = Vol. I.-III.
CO_2 = " II.-III.
N_2 = " IV.
$N = N_2 - N_1$ (reckoning N_1 = Air × 0·7905).
$V = R - N$.

(*e*) *Ethane along with Methane.*—Both together form the combustible constituent $V_1 = CH_4 + C_2H_6$. If hydrogen is present as well, we have $V_1 = V - H$.

Whilst methane by combustion furnishes its own volume of CO_2, the volumetric equation for ethane is—

$$C_2H_6 + 3\frac{1}{2}O_2 = 2CO_2 + 3H_2O.$$

Hence, if both hydrocarbons are present (V_1), the combustion yields a larger volume of CO_2, and to the excess corresponds according to the just given equation, an equal volume of ethane—

$$C_2H_6 = CO_2 - V_1,$$

and according to the first equation—

$$CH_4 = V_1 - C_2H_6.$$

METHODS OF COMBUSTION.

I.—*Ordinary Combustion.*

We need not go into details about this at this place, but we refer as an instance of this to the estimation of the sulphur compounds in coal-gas by the Drehschmidt method, *suprà*, p. 103.

II.—*Special Methods of Combustion.*

1. *By Explosion.*—The inflammation of an explosible gaseous mixture, suitably confined, by the electric spark, for the purpose

of estimating one or the other of the gases taking part in the explosion by means of the subsequent contraction, has been already applied by Volta for the estimation of oxygen in air by means of his endiometer; Bunsen (*Gasometriche Methoden*) has greatly improved and amplified this method, and Hempel, as we have already seen in a former chapter (pp. 96 *et seq.*), has made it specially serviceable for technical gas-analysis by means of his "explosion pipettes."

The explosion method is now principally applied to the estimation by combustion of *hydrogen* and of *methane*. We must, however, point out the following circumstances. Not every gaseous mixture containing these gases and the requisite quantity of oxygen can be straightway brought to explosion; it is sometimes necessary to add oxyhydrogen gas (electrolytically produced), or, when there is an excess of oxygen present, pure hydrogen. Nor can the simultaneous combustion of a little nitrogen be always avoided, as first pointed out by Bunsen, who prescribes preventing this by not employing more than from 22 to 64 vols. of combustion gases to 100 vols. of non-combustible gases. Pfeiffer (Lunge and Berl's *Untersuchungewmethoden*, 6th ed., vol. iii. p. 246) in the analysis of coal-gas employs 22 c.c. of the gases remaining after the treatment with absorbing agents (H, CH_4, CO, N) with 110 c.c. of air, which means about 52 vols. combustible gases to 100 vols. non-combustible gases.

The explosion method requires employing mercury as the confining liquid. Seger (*Tonindustrie Zeit.*, 1878, Nos. 25 and 26) has tried to avoid this by employing a special endiometer with water-seal and india-rubber taps, but this has never become popular. Much more success has been attained by Hempel, although he as well had to abandon his first attempts in that direction. Dennis (*Gas Analysis*, p. 147) describes a combustion pipette adapted to mercury as a confining liquid. The explosion arrangement has also been combined with an Orsat apparatus by Thörner (*Chem. Zeit.*, 1891, p. 763), but without much practical application.

The practical introduction of the explosion method into technical gas-analysis is in the first instance due to Hempel's new arrangements for that method. We have already in a former chapter (p. 96) described his new "explosion pipette," and we show his whole apparatus in Fig. 75. The pipette itself consists of the two strong tubulated glass bulbs, *a* and *b*, connected at the bottom by a canvas-covered rubber tube. The explosion bulb *a* is contracted at the top, like an ordinary gas-pipette, into a syphon-like capillary, closed by a pinchcock or glass rod, and is at the bottom closed by a glass tap *h*, which

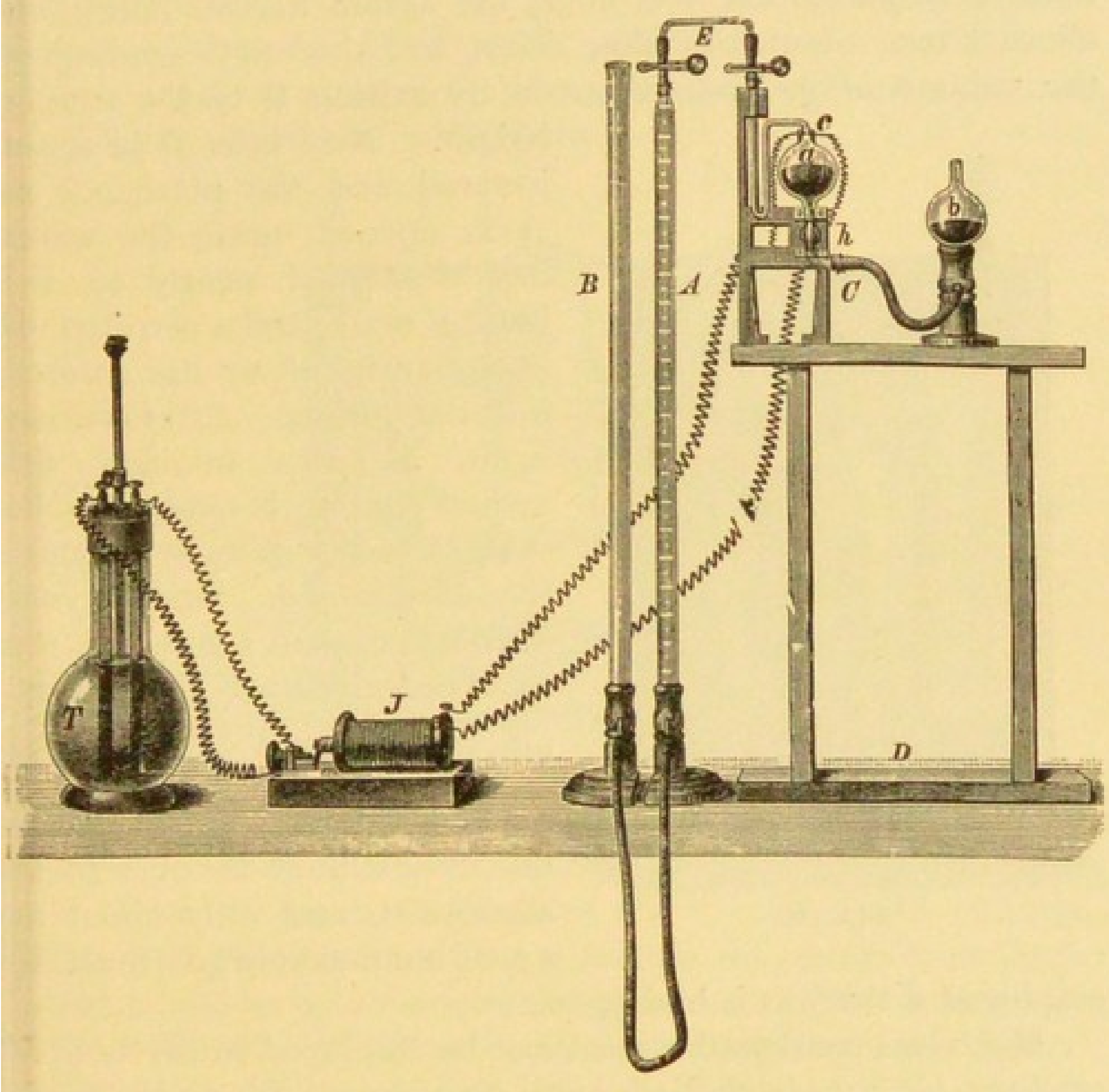

FIG. 75.

is connected with the "levelling bulb" *b* by the afore-mentioned rubber tube. At *c* two thin platinum wires are sealed into the contracted part of the bulb *a*, leaving a distance of 2 mm. between their ends, so that an induction-spark can pass through. For this purpose, the outer ends of the platinum wires are turned into loops and are connected by silk-covered copper spirals with the induction apparatus J, which receives its current from the battery T or any other source of electricity.

Both bulbs of the pipette are rather more than half-filled with mercury; if bulb *b* is lifted, tap *h* being open, *a* gets filled with mercury up to the capillary, and is kept in this state by closing tap *h*. In order to make a combustion, a suitable quantity of the gas to be burned is roughly measured off in the tube A of the Hempel burette, Fig. 75; the levelling tube B of the burette is placed on the floor, the water in the burette is allowed two minutes to flow down, and the exact reading of the volume of gas is now made by raising B to the proper height. Now tube B is again lowered and the pinchcock of A is opened, until the water has descended nearly to the bottom mark, and a corresponding quantity of air has entered into the burette. After waiting again for two minutes, the second reading is made and the volume of the gaseous mixture thus ascertained. Since 2 vols. *hydrogen* require 5 vols. air, 100 c.c. of the mixture should not contain more than $\frac{100 \times 2}{7} = 28{\cdot}57$ c.c. of hydrogen; but of course this utmost limit is never to be attempted, and only about 25 c.c. of combustible gas must be employed if this gas is hydrogen.

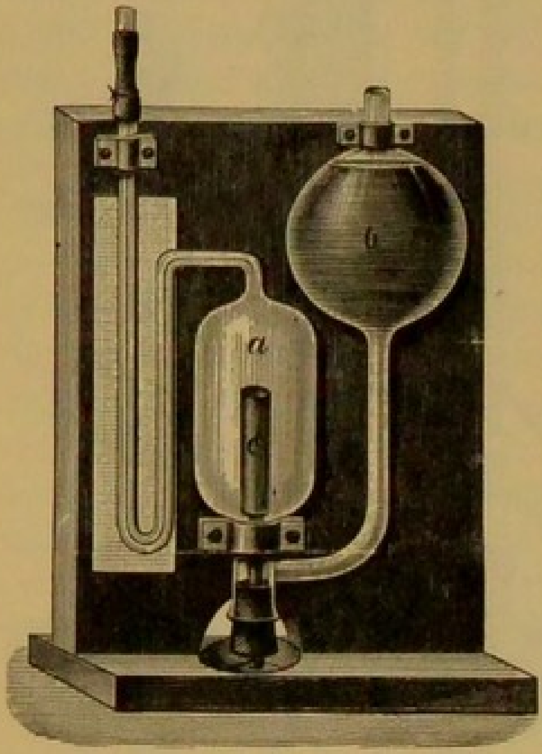

FIG. 76.

Much less combustible gas must be employed in the case of *methane*, for 2 vols. of this require 20 vols. air for combustion; hence 100 c.c. in the burette ought not to contain more than—

$$\frac{100 \times 2}{22} = 9{\cdot}09 \text{ c.c. methane.}$$

If the gaseous remainder, left after absorbing CO_2, O, CO, and the heavy hydrocarbons, contains too much nitrogen to enable it to explode after mixing with air, a sufficient amount of pure *hydrogen* must be added. This is best kept in stock in a Hempel's *simple hydrogen pipette*. This pipette, Fig. 76, is similar to the absorption pipette for solid reagents, shown in Fig. 51, p. 85, but into the bottom of bulb *a* a perforated zinc cylinder is introduced by means of a central glass rod passing through the bottom cork. Bulb *b* contains dilute sulphuric acid. After all air has been expelled from the apparatus, the side capillary is opened, whereupon hydrogen issues from it and is carried over into the gas-burette A, Fig. 75, in the well-known way. If the capillary is closed again, the hydrogen expended is renewed by the contact of the zinc with the sulphuric acid, and it forces the acid out of *a* into bulb *b*.

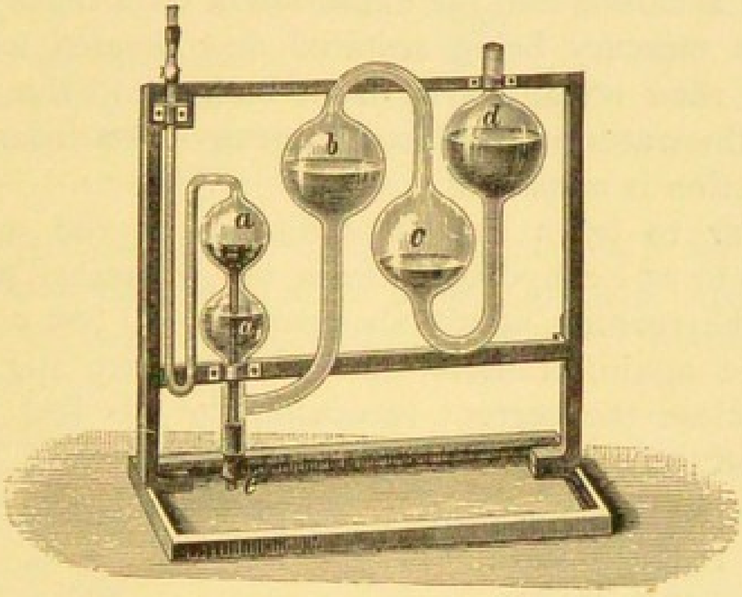

FIG. 77.

Fig. 77 shows Hempel's *composite hydrogen pipette.* The lower of the two superposed bulbs *a* and a_1 is filled with cuttings of pure zinc, mixed with a little platinum foil, the bottom neck being closed by a rubber-covered glass rod. Bulb *b* contains dilute sulphuric acid (1 : 10), introduced through the lateral capillary tube by means of a long funnel tube, during which process bulbs *b* and *c* are getting filled with hydrogen. At last a little mercury is poured into *d*, but for ordinary purposes this can be replaced by water.

The gas given off by these pipettes is never absolutely pure hydrogen, but contains a small amount of air, which, however, does not affect its use for the afore-mentioned purpose.

When the mixture of the combustible gas with air, and in case of need also with a measured quantity of hydrogen has been made, the explosion can be effected. The explosion pipette C, Fig. 75, p. 157, is placed on a stand D, bulb *a* is filled with mercury by raising *b*, and tap *h* is closed. The capillary of the pipette is connected by means of the capillary E with the gas-burette A, tap *h* is opened, and by lifting tube B, the pinchcocks being opened, the gaseous mixture is transferred from A into the explosion bulb *a*, whereupon the taps are again closed. Before closing tap *h*, it is best to lower bulb *b* and thus to produce a partial vacuum in *a*; but if the volume of gas in *a* is not large, and it is not highly explosive, tap *h* may even be left open. Now the battery T is put in motion, the current is closed, and the explosion at once takes place with a flash, the mercury being agitated and covered with a film. The gas is then retransferred from bulb *a* into the burette A, and after the water in the latter has run down from the sides, the contraction is measured.

In order to learn the manipulation of the method, we transfer 20 to 25 c.c. hydrogen from the hydrogen pipette into A, make the reading, admit air nearly up to 100 c.c., read off the volume again, transfer the mixture into the explosion pipette *a*, close the current, retransfer the gas into burette A, and read off the contraction. Example:

Hydrogen employed . . .	20·4 c.c.
Hydrogen + air	96·2 ,,
Hence air alone . . .	75·8 ,,
Containing oxygen . . .	15·2 ,,
Oxygen required by theory . .	10·2 ,,
Excess of oxygen . . .	5·0 ,,
Volume of gas after explosion . .	65·9 ,,
Contraction (96·2 – 65·9) . .	30·3 ,,

Found :—

$$\frac{30\cdot3 \times 2}{3} = 20\cdot20 \text{ c.c. hydrogen.}$$

We pass over to *the estimation of hydrogen in the presence of other gases, but in the absence of methane*, e.g., *in non-carburetted water-gas.*—Carbon dioxide and monoxide are successively removed and estimated (pp. 117 and 126), a measured portion of the gaseous remainder is mixed with at least two and a half times its volume of air, the mixture after measuring its volume is introduced into the explosion pipette, and the experiment finished as above.

Example:—

olume of water-gas employed . .	99·8 c.c.		
fter treatment by potash . .	95·7 „		
Contraction	4·1 „	= 4·12 per cent.	CO_2
fter two treatments by ammoniacal cuprous chloride, volume . .	56·0 „		
Contraction (95·7 − 56·0) . .	39·7 „	= 39·78 „	CO
aseous remainder employed for combustion (corresponding to 43·13 c.c. of the original gas) . .	24·2 „		
fter addition of air . . .	98·3 „		
Hence air admitted . . .	74·1 „		
Oxygen contained in this air .	14·8 „		
Nitrogen	59·3 „		
olume of gas after explosion . .	65·9 „		
Contraction (98·3 − 65·9) . .	32·4 „		
Corresponding to *hydrogen* in the gas	21·6 „	= 50·08 „	H
„ oxygen (from the air)	10·8 „		

The *nitrogen* contained in the original gas is equal to the ifference between the volume of the gas not absorbed by otash and cuprous chloride, and the volume of hydrogen found y combustion:—

Non-absorbed gas (= 43·13 c.c. of the original gas)	24·2 c.c.	
ydrogen contained therein . . .	21·6 „	
emainder (consisting of nitrogen) . .	2·6 „	= 6·02 per cent.

Final result:—

Carbon dioxide . .	4·12	per cent.	by volume
Carbon monoxide . .	39·78	„	„
Hydrogen . . .	50·08	„	„
Nitrogen . . .	6·02	„	„
	100·00		

Estimation of Methane in the Absence of Hydrogen, e.g., *in ire-damp.*—To such a mixture of methane and air a measured olume of pure hydrogen is added from a hydrogen pipette. If here is too little oxygen present more air (measured) is added, he whole is transferred into the explosion pipette, and the urrent closed. After this the gas is carried back into the gas-urette, measured, and the carbon dioxide formed (whose olume is equal to that of the original methane) is estimated by bsorption in caustic potash. This proceeding is safer than alculating the methane from the contraction after explosion, ince the hydrogen from the pipette is never pure.

Example :—

Gas employed	85·1 c.c.	
Gas + hydrogen	95·4 ,,	
Hydrogen alone	10·3 ,,	
Volume of gas after explosion	70·5 ,,	
After absorption by potash	65·7 ,,	
Contraction (= CO_2)	4·8 ,,	
Equal to methane	4·8 ,,	= 5·63 per cent.

Estimation of Hydrogen and Methane occurring together, e.g., *in Coal-gas, Producer-gas, Coke-oven Gas, Coal-pit Gases, etc.*—The absorbable gases (CO_2, O, CO, C_2H_4, etc.) are successively removed and estimated, as shown in previous chapters. Of the gaseous remainder, from 8 to 15 c.c. (according to whether there is more methane or more hydrogen present) is transferred into a Hempel's burette and measured, air is added nearly up to 100 c.c., the volume measured again, the mixture transferred into the explosion pipette, and the contraction by explosion ascertained. Now the volume of CO_2 formed is found by treating the gas in the caustic potash pipette; this volume is equal to that of the methane originally present, which on combustion causes a contraction of twice its volume (owing to the condensation of $2H_2O$ formed). By deducting this from the total contraction caused by the explosion, we find the contraction caused by the combustion of the hydrogen, two-thirds of which is equal to the volume of the hydrogen.

We shall revert to this subject later on when treating specially of methane.

A check test should be made to see whether sufficient air had been employed for combustion, by transferring the last remainder of gas to a phosphorus or pyrogallol pipette, which will show whether there is still oxygen in excess.

We give an example of the analysis of *coal-gas* :—

Gas employed		99·7 c.c.
After treatment by potash	95·9 c.c.	
Contraction	3·8 ,,	= 3·81 per cent. carbon dioxide
After treatment by fuming sulphuric acid and removal of the vapours by potash	91·2 ,,	
Contraction	4·7 ,,	= 4·71 ,, heavy hydrocarbons
After treatment by pyrogallol-potash	90·6 ,,	
Contraction	0·6 ,,	= 0·60 per cent. oxygen

After treatment by ammoniacal cuprous chloride	80·7 c.c.	
Contraction	9·9 ,,	= 9·93 per cent. carbon monoxide
Non-absorbed gas	80·7 ,,	
Of this employed for the combustion (=15·07 of original gas)	12·2 ,,	
Gas *plus* air	99·0 ,,	
Hence air alone	86·8 ,,	
Containing oxygen	17·4 ,,	
,, nitrogen	69·4 ,,	
Volume after explosion	79·0 ,,	
Total contraction (99·0 − 79·0)	20·0 ,,	
After treatment with potash	74·4 ,,	
Contraction (=CO_2)	4·6 ,,	
=Methane in 15·07 original gas	4·6 ,,	= 30·52 per cent. methane
Contraction caused by combustion of methane (4·6 × 2)	9·2 ,,	
Contraction caused by combustion of hydrogen (20·0 − 9·2)	10·8 ,,	
$\frac{2 \times 10{\cdot}8}{3}$	7·2 ,,	= 47·78 ,, hydrogen

Estimation of nitrogen :—

Unabsorbed gas employed (=15·07 per cent. of the original gas, as before)		12·2 c.c.	
Containing methane	4·6 c.c.		
,, hydrogen	7·2 c.c.		
	———	11·8 ,,	
Leaving a remainder of		0·4 ,,	= 2·65 per cent. nitrogen

Summary :—

Carbon dioxide	3·81	per cent.	by volume
Heavy hydrocarbons	4·71	,,	,,
Oxygen	0·60	,,	,,
Carbon monoxide	9·93	,,	,,
Methane	30·52	,,	,,
Hydrogen	47·78	,,	,,
Nitrogen	2·65	,,	,,
	100·00		

Pfeiffer's explosion-pipette, Fig. 78, admits of working with water in lieu of mercury, by avoiding the absorption of CO_2 by the water in the following manner :—Before the explosion, the water is drawn from the explosion bulb A into bulb B, for which purpose the taps *a* and *b* are provided. The peculiar arrangement of the platinum points in A avoids the formation of drops between them (*Chem. Zeit.*, 1904, p. 686. This pipette is supplied by H. Hörold, glass-blower, of Magdeburg). In order to avoid the squirting on the return of the confining water into A, after opening tap *b*, a drop of mercury is put into the connecting U-tube.

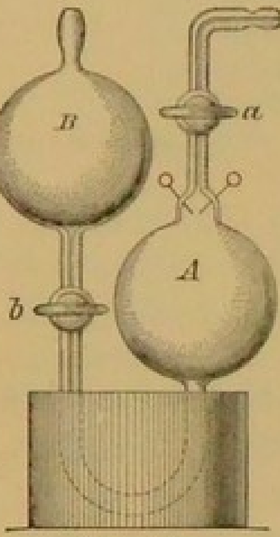

Fig. 78.

2. *Combustion by Means of Heated Platinum or Palladium.*—Several metals of the platinum group, viz., platinum, iridium, and especially palladium, have the property of causing the combustion of various gases by oxygen at temperatures below the point of inflammation, and that all the better, the finer the state of division and consequently the greater the surface offered by these metals to the gases. Especially easy and complete is the combustion of hydrogen, if mixed with a sufficient quantity of air and carried over gently heated, finely divided palladium. Under the same conditions carbon monoxide, ethylene, and benzene are burned with a little more difficulty, but also completely. Methane, however, whose temperature of inflammation is very high (about 790°) remains unchanged at moderately low temperatures. From this follows the possibility of estimating the more easily burning gases, especially hydrogen, in the presence of methane by means of *fractional combustion.*

The first to apply fractional combustion for this purpose was W. Henry (*Annals of Philosophy*, xxv. p. 428), who employed platinum sponge heated to 177°, but his proposal did not lead to practical results in gas-analysis. This only ensued on the labours of Clemens Winkler, who published his method, founded on the application of finely divided palladium in the shape of "palladium asbestos," in 1877, in his *Anleitung zur Untersuchung der Industrie-Gase*," ii. pp. 257 *et seq.* Later on Bunte (*Ber.*, 1878, p. 1123) proposed palladium wire, Hempel (*Ber.*, 1879, p 1006) superficially oxidised palladium sponge at a temperature of 100°. Winkler's method has, however, remained victorious, and his palladium asbestos is employed in most of the modern apparatus for technical gas-analysis, *e.g.*, in the Orsat-Lunge (p. 71).

Winkler's combustion apparatus consists of a short glass capillary tube, bent at each end in a right angle, into which a fibre of asbestos, impregnated with finely-divided asbestos, has been loosely introduced, so that it does not impede the passage of the gas. This *palladium asbestos* is prepared in the following way:—Dissolve 1 g. palladium in aqua regia, evaporate the solution on a water-bath to dryness, whereby any adhering hydrogen chloride should be removed as completely as possible, and dissolve the palladium chloride thus produced in a little water. (Or else employ a solution of 3 g. sodium palladium protochloride in a small quantity of water.) Add a few cubic centimetres of a cold saturated solution of sodium formate and sufficient sodium carbonate to produce a strongly alkaline reaction. Now introduce 1 g. of very soft, long-fibred asbestos, which, if any unnecessary excess of water has been avoided, absorbs the whole liquid, forming a thick paste. This is dried at a gentle heat, by which process black, finely divided palladium is uniformly precipitated upon the asbestos fibre. In order to make the palladium adhere upon the asbestos, the product thus prepared is heated on a water-bath till completely dry, put into a glass funnel and freed from all adhering salts by thorough washing, no palladium being removed. After drying, the substance shows a dark grey colour, with a slight tendency to stain the fingers on being touched, and contains about 50 per cent. palladium. It possesses a very high degree of chemical activity; in the perfectly dry state it causes the combination of hydrogen and oxygen even at the ordinary temperature, but to make sure of attaining this it is always employed in the heated state. (The same process is employed for preparing *platinum* asbestos, required for other purposes, but this is generally made with only 10 to 25 per cent. platinum.)

In the place of the palladium asbestos, which easily shifts its place in the capillary tube, Leutold (as communicated to Treadwell, Lehrbuch, etc., vol. ii. p. 545) applies a spiral of palladium wire.

The tubes for receiving the palladium asbestos are capillary glass tubes, about 1 mm. bore and 6 mm. outside diameter, cut in pieces 16 or 18 cm. long. The asbestos fibre is introduced into them in the following way:—A few loose fibres of the palladium asbestos are laid alongside each other on smooth filtering paper up to a length of 4 cm. They are moistened with a few drops of water, and, by passing the finger over them, are twisted into a fine, straight thread, which in the moist state has the thickness of a stout sewing cotton. This thread is grasped at one end with the nippers, and, without bending or nicking, is slid from above into the (vertically held) capillary tube. This tube is then filled with water, and by jerking or drawing this off at the ends, the asbestos thread is brought into the centre of the tube, which is now dried in a warm place. When dry, the ends are bent off at a right angle for a length of 35 or 40 mm., and the edges rounded off with the lamp. (The dealers in chemical apparatus supply capillaries already charged with palladium asbestos.)

Manipulation.—The volume of the combustible gas contained in the gas-burette A, Fig. 79, is read off; it should in no case exceed 25 c.c. The levelling tube is placed on the floor of the room, and by opening the pinchcock, enough air is admitted to bring up the total volume of the gas to nearly, but not quite, 100 c.c. When all the water has run together, the volume of the gas is read off. The capillary tube E is now placed between the burette A and the pipette C, and heated for one or two minutes by means of the small gas-jet F (or a spirit-lamp); but not too much, certainly not to a visible red heat, or until the glass softens. The combustion can now begin by elevating the levelling tube, opening the pinchcocks, and passing the gaseous mixture in a slow stream through the heated palladium asbestos into the pipette C. That end of the asbestos thread which is opposite to the entrance of the gaseous current begins to glow visibly, and this glowing frequently reappears when conveying the gas back into the burette. All the time the flame is left burning under the capillary tube, taking care not to pass the gas through too quickly, and that no drops of water should get into the capillary, which would then be sure to crack. In the case of easily burning gases, the combustion is generally finished by passing the gas twice forward and backward; but in any case we have to make sure by another passage that no further contraction takes place. The remaining gas is measured, and the contraction produced is thus ascertained.

From this the quantity of the gas burned is calculated, either directly, or after removing any carbon dioxide formed by the combustion, and ascertaining the decrease of volume thus produced.

By this method *hydrogen* is burned very easily and quickly; *carbon monoxide* a little less easily, but still quite conveniently; *ethylene*, *acetylene*, and *benzene* more slowly, and only by heating more strongly. *Methane* is not burned at all; even when a considerable excess of easily combustible gases is present, no methane, or at most only extremely slight traces of it is burned with them, according to Winkler. But if the temperature rises too much, a little methane is burned as well. In fact Treadwell (*Lehrb. d. quant. Analyse*, 4th ed., p. 575) finds that the results are generally too high by 0·5 to 1 per cent. On the strength of only two experiments Charitschkow (*Chem. Centr.* 1903, i. p. 295) even asserted that Winkler's method does not admit of anything like the exact separation of hydrogen and methane; but Brunck (*Z. angew. Chem.*, 1903, p. 695) proved this assertion to be entirely wrong, and found Winkler's method to be quite correct, if carried out as prescribed by its author

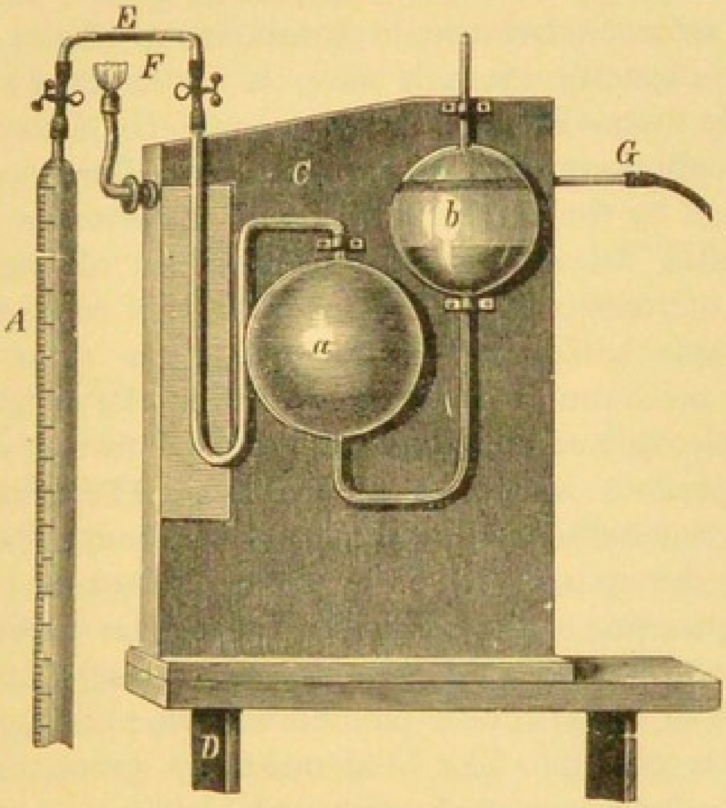

FIG. 79.

(and *suprà*). In no case must *oxygen* be employed for the combustion in the place of air, because in this case a portion of the methane would be burned as well (Brandt, *Z. angew. Chem.*, 1903, p. 695).

A very complete investigation of the combustion by means of the *catalytic action of hot palladium* has been made in Bunte's laboratory by Richardt (*J. Gasbeleucht.*, 1904, pp. 566 *et seq.* and 590 *et seq.*), who in the beginning of his paper enumerates the very extensive literature on this subject. He employed, as Bunte had previously done, palladium in the state of a solid wire in lieu of palladium asbestos, because, in consequence of the good heat-conducting capacity of such wire, it is easier to avoid any considerable inequalities of temperature. He found, as Haber had previously done, that at temperatures below 450° methane is not burned by the catalytic action of palladium wire. Above 450°, and still below a visible red heat, in all cases notable quantities of methane are burned, if the contact with the catalyser lasts sufficiently long. During a short contact a current of methane and air passes over the palladium wire without noticeable combustion even at 600° to 650°, whilst any hydrogen present is completely burned. The combustion of methane is not influenced by that of hydrogen, even in a slow passage of the gases. In order to carry out an analysis, a measured quantity of the combustible gases is mixed with air and is passed through a tube, heated by a small Bunsen burner in the midst of which tube a palladium wire, plied several times upon itself, is placed. The heat must *not* go up to the point where the palladium wire shows a red glowing, because in this case notable quantities of methane are burned. Bunte has found that the proper temperature is reached when the Bunsen flame begins to exhibit the coloration due to the potassium or sodium contained in the glass of the capillary, which in the case of pretty high-fusible glass takes place at a temperature of 550° to 600°. At this temperature no methane but all the hydrogen is burned. To make sure of the completeness of the combustion, the gas may be passed a second time over the palladium, in which operation the temperature may be kept rather higher, since now, after the hydrogen is removed, there is no danger of any methane getting burned. *Ethane* behaves similarly to methane, and these two hydrocarbons cannot be separated by fractional combustion. *Ethylene* begins to burn already at 300°, but it cannot be estimated by fractional combustion in a mixture with ethane or methane, because, in order to burn it quantitatively, a temperature must be employed at which methane is already beginning to burn. The estimation of ethylene is most simply carried out by treatment of the gas with bromine water (*cf.* p. 119).

Philip and Steele (B. P. 27281 of 1911) describe the construction and operation of a draught-proof catalytic combustible *gas-detector*, comprising a wire adapted to be heated by the catalytic combustion of the gas to be tested, and means for indicating the resulting change in the resistance of the wire.

L. A. Levy (*J. Gas Lighting*, cxxii. p. 524) employs an electrically heated platinum spiral, followed by a quartz capillary.

The *fractional combustion* of mixtures of hydrogen and methane with air by the action of heated palladium has been already described *suprà*, pp. 71 *et seq.*, as carried out by means of the Orsat-Lunge apparatus.

Bunte gives the following prescriptions for carrying out the fractional combustion of such gaseous mixtures when employing his burette, described *suprà*, pp. 58 *et seq.* Besides this burette A, a second burette B is required. In the burette A 22 to 25 c.c. of the non-absorbable gases are measured off and mixed with the air required for combustion. For this purpose first the lower tap is opened, then the upper tap in such manner that it is in communication with the outer air, which now enters as the water is running out. When the water level has gone down to about 5 c.c. below O, first the upper tap is quickly closed, then the lower tap, the gases are mixed by shaking the burette, the pressure is made equal to that of the atmosphere, *plus* the column of water in the funnel, and the reading is taken. Now burette B is filled with water up to the capillary tube, and both three-way taps are connected with the interposition of a *palladium tube* C. This tube is made of glass of high-fusing point, 10 cm. long, 5 mm. wide outside diameter, and 3 mm. wide. The palladium wire is 100 mm. long, 0·5 mm. thick; it is plied four times upon itself and introduced into the tube up to the centre. This place is now narrowed by heating the tube up to getting soft, so that the wire is held fast here;

the remaining portion of the tube is loosely filled with long-fibred asbestos (see Fig. 80). Tube C_1 is connected with the burettes A and B by short, thick-walled rubber tubes.

Now both three-way taps are turned so that none of their bores are open; the funnel of burette A is filled with water; by briefly opening its lower tap, the pressure in it is reduced; both three-way taps are at the same time quickly turned in such manner that the palladium pipe communicates with the interior space of both burettes, and C is heated, whereby the air is expanded and forces the water from the top capillaries back into the burettes. The rubber tube of the pressure bottle is connected with the bottom tap of A, this tap is opened, tube C is heated at the contracted place until the small flame turns yellow, and the bottom tap of B is opened so far that the gas travels in a moderately fast stream from A through C into B. The water should flow out of B in a jet, not in drops, and the palladium wire at the entrance end of the gas is not to turn red-hot (because in that case a little methane would be burned as well). At the moment when the water in burette A has got up to the top, first its bottom tap, then that of B is closed, and the gas is in the same way as before carried back from B into A; here, after cooling, the pressure is made normal, the reading is taken, and thereby the contraction is ascertained.

FIG. 80.

Example:—

Volume of the gaseous remainder from 100 c.c. coal-gas, after absorbing CO_2, heavy hydrocarbons, oxygen, and carbon monoxide	85·0 c.c.
Employed of this for combustion	22·2 „
Volume after dilution with air	105·3 „
„ combustion	19·0 „
Contraction calculated on the original volume $\frac{19\cdot0\times85\cdot0}{22\cdot2}$	72·8 „
Corresponding to $\frac{2\times72\cdot8}{3}$ hydrogen	48·5 „

As a control, the oxygen left after the explosion is determined; its volume should be equal to one-third of the contraction.

Methane is estimated (together with hydrogen) in the same gaseous remainder from the absorbing operations in Bunte's *explosion burette*, *i.e.*, a Bunte burette with platinum points fused in near the top. In this 12 to 15 c.c. of the gas is measured off, an excess of air is drawn in, mixed by shaking, measured, the water level is lowered, the explosion is effected by an electric spark, the contraction is read off, 1 or 2 c.c. of caustic potash solution is run down along the glass walls, water is slowly allowed to get in, the pressure is again made normal, and the "total contraction" (due to the formation of CO_2 and H_2O) is ascertained. Deducting therefrom the amount due to the combustion of hydrogen (as ascertained *suprà*), one-third of the remaining contraction indicates the volume of the methane, since for each volume of this 2 vols. of oxygen have vanished.

Example:—

Gaseous remainder employed (from 85 c.c., left after absorbing CO_2, C_mH_n, O_2, and CO_2) . . .	12·7 c.c.
Volume after adding air	104·1 ,,
Hence air added	91·4 ,,
Volume after explosion	78·9 ,,
Hence total contraction	25·2 ,,
The same calculated on the whole gas $\frac{85 \times 25\cdot2}{12\cdot7}$ . .	168·8 ,,
Deducting therefrom the 72·2 due to the combustion of hydrogen, as found *suprà*, remain . . .	96·0 ,,
One-third of which indicates the methane . . .	32·0 per cent.

In cases where the gas remaining after the absorption of CO_2, illuminants O and CO, is too poor to be exploded without the addition of hydrogen, Vail (*J. Ind. and Eng. Chem.*, 1913, p. 756) recommends enriching it by the formation of hydrogen and oxygen by means of an electric arch, after addition of water for that purpose.

Felser (Ger. P. 266046) describes an apparatus for ascertaining the incomplete combustion of fire-gases by effecting the complete combustion by means of a catalytical substance (platinum coated with palladium), interposed between two thermo-elements, so that the rise of temperature after the complete combustion can be measured and catalysed for estimating the combustible gases originally present.

3. *Combustion of Methane by Heated Platinum.*—This method has been already described in connection with Hempel's (*suprà* p. 92) and Drehschmidt's apparatus (*suprà* p. 103). We shall later on describe its application to the testing of the air of coal-pits by Coquillion's Grisoumeter and other apparatus.

4. *Combustion of Nitrogen by Oxygen through the Action of Electric Sparks.*—This process has been first employed by Lord Rayleigh. Henrich and Eichhorn (*Z. angew. Chem.*, 1912, p. 468) describe an arrangement of apparatus, by which free nitrogen can be comparatively quickly removed quantitatively from gaseous mixtures through the action of electric sparks in the presence of oxygen and of caustic soda solution which absorbs the nitrogen oxides formed.

5. *Combustion by Cupric Oxide.*—This method, which is due to Jaeger (*J. Gasbeleucht.*, 1898, p. 764), depends upon the fractional combustion of the mixture of gases by cupric oxide at varying temperatures. As the oxygen required for the combustion is not added in the gaseous form, but is furnished by CuO, the relations of the volume changes are very simple. The hydrogen disappears completely on burning and its volume is equal to the contraction; methane forms its own volume of carbon dioxide, which is easily measured by absorption. The cupric oxide is placed in a small tube of the form shown in Fig. 81, which is made of hard Jena glass,[1] with a capillary on one side and a somewhat wider tube on the other. To fill the tube, large grained cupric oxide is introduced, so that it lies at the beginning of the capillary, and a plug of asbestos fibre placed against it; the wide part of the tube is then filled with freshly ignited, powdered cupric

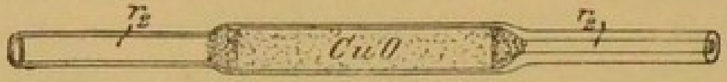

FIG. 81.

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[1] Since glass are easily bent by heating and crack when a drop of water gets in, Knorre (*Chem. Zeit.*, 1909, No. 79) employs tubes of *quartz*-glass, 10 cm. long, 5 mm. wide, and 0·5 to 0·75 thickness of the walls (supplied by Dr Siebert & Kühn, of Kassel).

oxide, which is kept in position by a second plug of asbestos. The tube is connected by rubber tubing on one side with the measuring burette, and on the other side with the absorption pipette, charged with potassium hydroxide solution. For the combustion of the hydrogen the tube is heated to 250°; this temperature is controlled by means of a thermometer, the bulb of which is placed close against the tube. After oxidising the hydrogen and reading the contraction, the thermometer is removed and the methane then oxidised by heating the cupric oxide to a red heat. As the carbon dioxide formed is absorbed by the potassium hydroxide in the pipette, the reduction of volume indicates the volume of the methane directly.

The combustion with cupric oxide has the great advantage over other methods that the whole of the gas left after absorption can be taken for the determination, so that any errors do not influence the final result to the same extent as when only a fraction of the residue is used. There is, however, the drawback that the methane is not easily burnt completely, and that the temperature of combustion is so high, since the tube must be allowed to cool down before reading the volume; the reduced copper must also be oxidised after each analysis.

The apparatus employed by Jaeger is shown in Fig. 82. The burette is a modified form of that of Bunte, narrowed at the top to permit of more accurate readings, and provided with a lateral exit-tube; it is enclosed in a water-jacket. The absorptions are carried out with Hempel pipettes in the usual way. For the fractional combustion of the hydrogen and methane, the cupric oxide tube is connected by rubber tubes s with the burette, and by s_2 (both of them bound with wire) with a Hempel pipette filled with potassium hydroxide solution. Below the combustion tube is placed the Bunsen burner b, which is provided with a special regulating-tap and a fan-shaped fitting to the burner. A framework of sheet iron attached to the burner carries a cover in which a short thermometer, graduated up to 270°, is fixed so that its side lies close to the side of the combustion tube. At the beginning of the test the solution in the pipette is forced up to the mark m of the capillary by blowing through the tube s_3 while the upper burette cock is in the position I; this stopcock is then closed by a quarter turn (position III), and the tube slowly heated to

250° and kept at this temperature with as little variation as possible. As soon as this temperature has been reached, the upper stopcock of the burette is opened (position II), then the lower one and the levelling bottle raised. By passing the gas

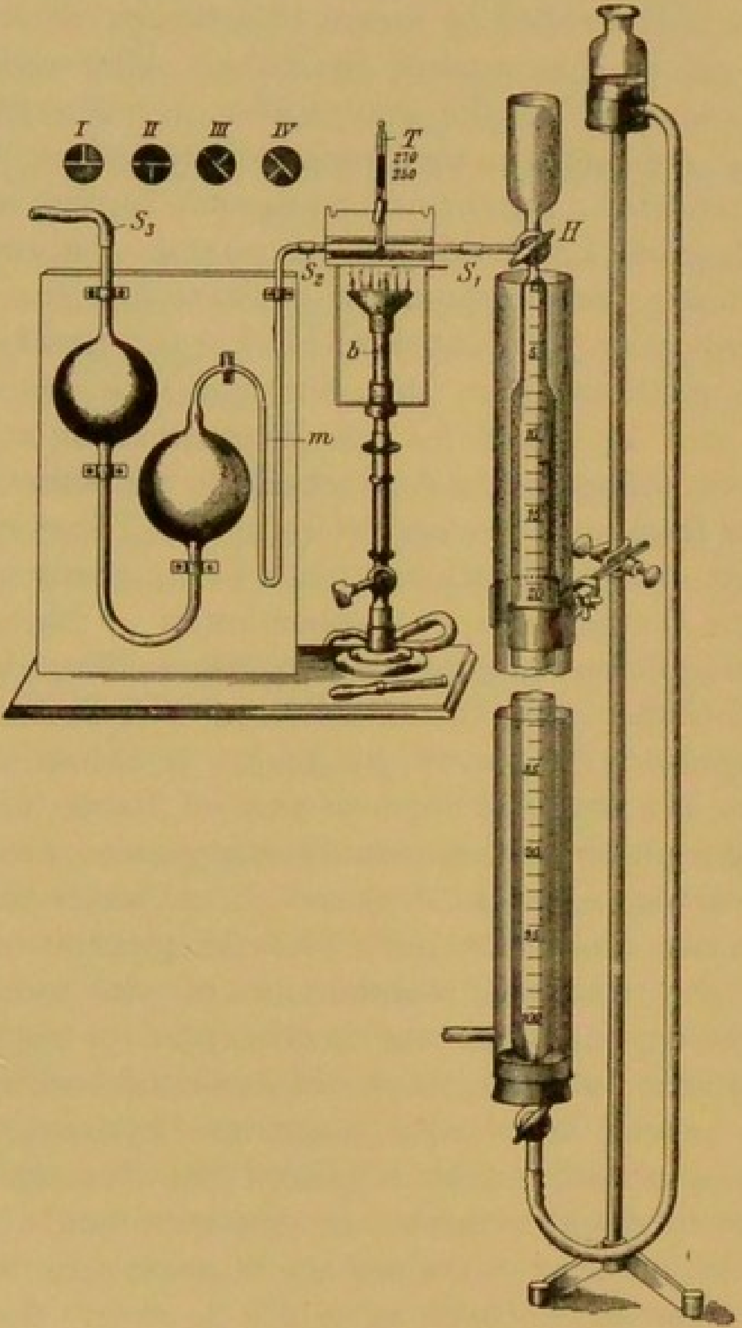

FIG. 82.

slowly from the burette to the pipette and back again, the *hydrogen* is completely oxidised. After allowing to cool, the water in the pipette is again brought to the mark *m*, and the residual gas measured.

A correction has to be applied for the oxygen of the air initially enclosed in the combustion tube, which participates in the oxidation of the hydrogen. This is made once for all by filling the burette with pure hydrogen and determining the value of the correction; it amounts to about 0·5, and must be subtracted from the hydrogen contraction found in the subsequent testings. This correction must also be made in the determination of the nitrogen at the end of the analysis.

For the subsequent combustion of the *methane*, the cover with thermometer over the combustion tube is removed, the tube heated with a more powerful flame to a bright red heat, and the gas repeatedly carried over the cupric oxide, till no further decrease in volume takes place. The carbon dioxide formed by the combustion is retained in the alkali pipette; the decrease in volume, therefore, corresponds directly (without correction) to the methane present. The residual gas must be allowed to cool completely to the temperature of the room before taking the final reading.

The incombustible gas residue, increased by the volume of the oxygen previously enclosed in the cupric oxide tube and afterwards consumed (correction-value), gives the *nitrogen* content of the air.

For the determination of the percentage of *nitrogen only* in a sample of gas, the latter is introduced into the burette, the cupric oxide tube at once heated to a high temperature, and the gas passed backwards and forwards into the potash pipette until no further contraction occurs. The whole of the gaseous constituents, other than nitrogen, are thus completely removed, and the residual volume of gas, read after complete cooling, plus the previously ascertained correction for the oxygen content of the cupric oxide tube, gives directly the amount of nitrogen in the gas, and its percentage if 100 c.c. have been taken. Where many such tests have to be made, it is convenient to displace the air in the cupric oxide tube by nitrogen previous to the test, in which case no correction is necessary.

After each test the cupric oxide tube must be heated in a current of air to reoxidise the reduced copper.

The results of this method are satisfactory as regards accuracy. The combustion of the methane is, however, very slow, and varies greatly according to the physical condition of the oxide of copper.

Cupric oxide is also used by Winkler in his apparatus for the estimation of methane in pit air, which will be described later on. Other apparatus for burning gases by means of cupric oxide have been described by Ubbelohde and de Castro (*J. Gasbeleucht.*, 1911, p. 810); Hohensee (*ibid.*, 1911, p. 814); Worrell (*Metallurg. Chem. Engin.*, 1911, p. 576; *Z. angew. Chem.*, 1912, p. 915); the "Metrogas" apparatus (*J. Gas Lighting*, 1911, p. 819); Dennis (his *Gas Analysis*, p. 201).

Grebel's "comburimeter" (*J. Gas Lighting.*, cxxi. p. 738) measures the quantity of air or oxygen required for burning the gas, by means of a special instrument, the "comburimeter," consisting of a burner with chimney, with exactly regulated supply of air and gas, in which an excess of oxygen in the flame is recognised by the change of colour of a drop of melted lead.

IV. Gas-Analysis by Optical and Acoustical Methods.

A large number of chemists and physicists, beginning from Dulong in 1826,[1] have studied the optical behaviour of gases, and more especially their refractometric properties. We owe it, however, only to the labours of Professor Haber and his students, that these properties have led to practical results for the purpose of scientific and technical gas-analysis.

Haber's *gas-refractometer* (supplied by Carl Zeiss, of Jena) is constructed on the principles laid down by Lord Rayleigh (*Proc. Roy. Soc.*, 1896, p. 203) and Ramsay and Travers (*ibid.*, 1897, p. 225), but many difficulties had to be overcome before an instrument fit for practical use had been worked out. This instrument has been described by Haber in *Z. angew. Chem.*, 1906, p. 1418, and in *Z. Elektrochem.*, 1907, p. 460. A long paper by Stuckert (*ibid.*, 1910, pp. 37 to 75) describes the researches made by means of this with a number of gases. We refrain, however, from going into this, as Haber has later on, in conjunction with Dr Löwe, of the firm of Carl Zeiss, worked out another

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[1] The literature of this subject is enumerated in the paper of Stuckert, mentioned in the text.

nstrument which is much more easily manipulated, especially or technical purposes. This instrument, called *interferometer*, described by Haber and Löwe in *Z. Elektrochem.*, 1910, p. 1393 *et seq.*[1] It aims at replacing Lord Rayleigh's method f measuring the refraction, where the changes in the composi-on of the gas to be examined are compensated by alterations f its pressure, by a more easily manipulated method, which is ndependent of the thermometric and barometric oscillations, nd admits of a continuous observation of the composition of the aseous current. This object has been attained by combining ith the instrument an optical compensator, which renders the anipulation extremely simple, the only part to be moved eing the measuring screw of the compensator. It can be dapted to very different degrees of accuracy, according to the equirements of the case; up to $\frac{1}{50}$ per cent. of CO_2 in the air of its, etc. We must refer for the details to the original, and we nly mention that the principal applications for which this nstrument is intended are the examination of the air of coal-its, of the purity of the hydrogen intended for aeronautic urposes, of coal-gas carburetted with benzol, of the percentage f ammonia in air obtained by synthetical processes, of the CO_2 nd SO_2 in smoke-gases. Ottomar Wolff (*Chem. Zeit.*, 1914, . 349) points out some precautions to be taken in gauging as-interferometers.

Mohr (*Z. angew. Chem.*, 1912, pp. 1313 *et seq.*) has made n investigation of the application of the interferometer for the echnical examination of smoke-gases, and found it useful for hat purpose, more especially for the estimation of carbon ioxide, but not so much for that of carbon monoxide.

Gas-analysis by positive rays has been proposed by J. J. Thomson, and by J. E. Verschaffelt (*Bull. Soc. Chim. Belg.*, 913, p. 52). This method does not belong to the domain of *chnical* gas-analysis.

Marc Landau (*Comptes rend.*, clv. p. 403) employs the nergy of light for gas-analysis, especially for polymerising non-aturated hydrocarbons, *e.g.*, ethylene and acetylene. The aseous mixture is exposed to ultra-violet rays, and the ontraction of volume is measured. In the presence of oxygen he energy of light, such as that of a mercurial vapour quartz

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[1] It can be obtained from Carl Zeiss in Jena.

lamp, converts substances containing carbon and hydrogen into carbon dioxide and water.

The application of *acoustical* methods for the detection of small quantities of methane in the air of pits, etc., will be described later on *sub* "methane."

V. SEPARATION OF GASES BY LOW TEMPERATURES.

Methods for this pupose have been worked out by Ramsay and Travers (Travers, *The Experimental Study of Gases*); by Hempel (*Gasanal. Methoden*, 4th ed., p. 119); by Erdmann (*Berl. Ber.*, 1910, p. 1702).

Lebeau and Damiens (*Comptes rend.*, clvi. p. 797 and clvii. p. 144; *Am. Abstr.*, 1913, p. 2109) effect the analysis of illuminating gas by subjecting the gas to low temperatures produced by means of liquid air, or of solid carbon dioxide and acetone, or of petroleum spirit cooled by liquid air, and thus freezing out the condensable gases: carbon dioxide, aqueous vapour, the saturated homologues of ethane, ethylene, and acetylene; the non-condensable residue consists of hydrogen, methane, carbon monoxide, nitrogen, and oxygen. Each fraction is then submitted to a process of extraction or fractionation. The determination of nitrogen is direct, not by difference. As much as 1000 litres of gas was taken for a single analysis, and this method is asserted to admit of the most complete analysis of illuminating gas ever made. This method is highly commended by Czakó (*J. Gasbeleucht.*, 1913, p. 1192). By this process hydrogen cannot be separated from methane, but from ethane, propane, etc.

VI ESTIMATION OF THE SPECIFIC GRAVITY OF GASES.

In many cases the specific gravity of gaseous mixtures admits of drawing a conclusion as to their composition. In the manufacture of illuminating gas, for instance, where in the different stages of the process very different products are formed, the specific gravity is checked throughout. It can also be made available for checking the quality of furnace-gases, of pyrites-kiln gases, and similar cases.

In all well-conducted coal-gas works a continuous record of the specific gravity of the gas produced is made, which is not merely of statistical value, but also gives some information concerning changes in the composition of the gas. It must, however, be borne in mind that changes in the specific gravity of the gas are no certain indication of its quality. Thus, for instance, the specific gravities of ethylene and of nitrogen are almost identical.

Apart from affording indications as to the chemical composition, a constant check of the specific gravity of illuminating gas is important for the manufacturing process, because the quantity of gas issuing from a small orifice at constant pressure (as in the Welsbach burner) varies indirectly with the square root of its specific gravity, and the same holds good with regard to the capacity of the mains for the delivery of gas under constant pressure. This is sometimes noticed in a very disagreeable manner when changing the gas supply from ordinary coal-gas to water-gas, their specific gravities differing so very much, say about 0·65 the former and 0·38 the latter. Where districts of very different level have to be supplied, it must be also taken into account that the relative pressure of gas increases with increasing altitude, the increase being greater the lower the specific gravity of the gas.

In the use of coal-gas for the filling of *balloons*, its specific gravity is, of course, of primary importance.

(a) *Calculation of the Specific Gravity from the Analysis.*

The specific gravity of a gaseous mixture can be calculated from the analysis by multiplying the percentage content of the single gases with their specific gravities, and dividing the sum by 100, according to the formula:

$$0.0696H_2 + 0.9673CO + 0.5538CH_4 + 1.0C_nH_{2n} + 2.8C_nH_{2n-6} + 1.5201CO_2 + 1.1055O_2 + 0.9680N_2)\,\frac{1}{100}.$$

This presupposes a knowledge of the composition of the gas. Hence it is mostly necessary to employ one of the other methods for estimating the specific gravity. But if this is known, the formula, according to Pfeiffer, may render valuable service for estimating *the specific gravity of the total heavy hydrocarbons* (C_nH_m), and further the volume-percentage of benzene and the caloric value. If we signify by S the experimentally found specific gravity of the total gas, and by s the specific gravity of the heavy hydrocarbons, we have:

$$s = [100S - (0{\cdot}0696H_2 + 0{\cdot}9673CO + 0{\cdot}5538CH_4 + 1{\cdot}5201CO_2 + 1{\cdot}1055O_2 + 0{\cdot}9680N_2)\frac{1}{C_nH_m}.$$

For instance:—

	Per cent. by vol.	Sp. gr.
H_2	$= 55{\cdot}5 \times 0{\cdot}0696$	3·861
CO	$= 8{\cdot}4 \times 0{\cdot}9673$	8·102
CH_4	$= 29{\cdot}7 \times 0{\cdot}5538$	16·400
CO_2	$= 1{\cdot}7 \times 1{\cdot}5201$	2·583
O_2	$= 0{\cdot}19 \times 1{\cdot}1055$	0·210
N_2	$= 1{\cdot}2 \times 0{\cdot}9680$	1·161
		32·317
Specific gravity of the gas (S)		0·3855
Percentage of C_nH_m		3·3
Hence $S = \frac{38{\cdot}55 - 32{\cdot}32}{3{\cdot}3}$		1·888

For accurate determinations, the well-known method of Dumas (directly weighing the gas in glass vessels of known capacity) can be employed. For technical purposes, however, simpler methods are used which will now be described.

(b) *Determination of the Specific Gravity of a Gas by measuring its Velocity when issuing from an Orifice* (*Apparatus of Schilling*).

This method, devised by Bunsen (*Gasometrische Methoden*, 2nd ed., 1877, p. 184), is founded on the different rates of effusion of equal gas volumes through a fine opening, the squares of the time of effusion showing the relation of the specific gravities. If a gas of specific gravity s has the time of effusion t, and another gas of specific gravity s_1 the effusion-time t_1, the relation is:

$$\frac{s_1}{s} = \frac{t_1^2}{t^2}.$$

When comparing a special gas with air, as is always done in practical work, the specific gravity s of the air is put $= 1$, and is thus eliminated from the calculation. If the time of ffusion of the other gas is $= g$ seconds, and that of an equal volume of air $= l$ seconds, the specific gravity of the other gas is found by the formula:

$$s_1 = \frac{g^2}{l^2}.$$

The apparatus employed by Bunsen is too delicate for technical work, but its principle has been made use of by H. N. Schilling (*Handb. d. Steinkohlengasbeleuchtung*, 3rd ed., p. 100), whose apparatus is so convenient that it has found universal application, not merely for coal-gas, but also for all other gases or gaseous mixtures sparingly soluble in water.

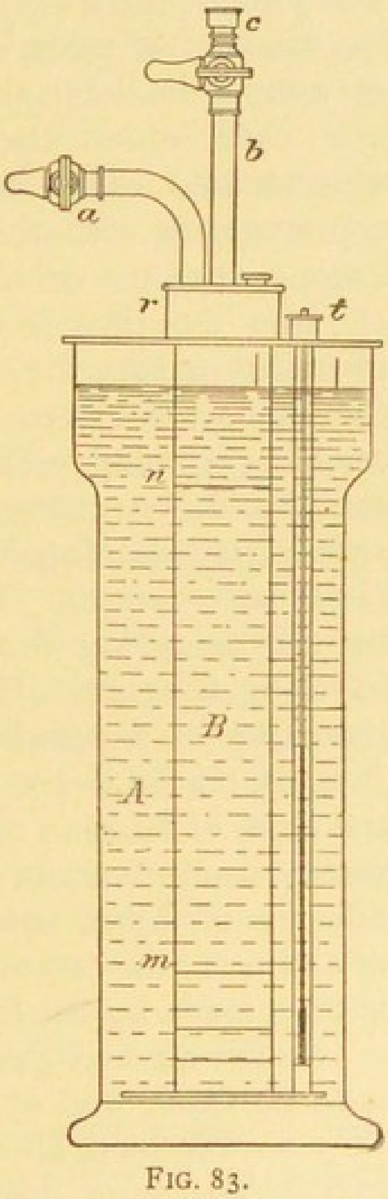


FIG. 83.

Schilling's apparatus, shown in Fig. 83, consists of a glass cylinder B, 40 mm. wide inside and 450 mm. high. Its upper end is cemented into a brass cover through which passes the inlet-pipe *a*; the outlet-pipe *b* passes through the centre of the cover. Pipe *a* is a brass tube 3 mm. wide, turning on the outside in a right angle and provided with a stopcock; it is connected with the source of the gas by a rubber tube. The outlet-pipe *b* is 12 mm. wide, and is closed at the top by a disc of thin platinum foil *c*, in the centre of which a small hole has been made by means of a very fine needle and afterwards hammered out, thus forming the orifice for the issuing of the gas. To protect it from dust, a cap is screwed on *c* when the apparatus is not in use. Tube *b* can be shut by a three-way tap, between the orifice and the cylinder, which can be turned so as to communicate either with *b* or *c*. The outer cylinder A, 125 mm. wide, is filled with water nearly up to the top, when the inner cylinder, filled with gas, is immersed in it. This height of water is shown by a mark on the glass.

The inner cylinder B has two marks, *m* and *n*, running all round, 300 mm. distant from each other, *m* being 60 mm. distant from the bottom of cylinder B. This cylinder is open at the bottom, resting on a metal foot, and is kept in position at the top by a metal frame *r*, which rests with three arms on the rim of cylinder A and also carries the thermometer *t*.

To make a determination, A is filled with so much water that there is just sufficient room for introducing cylinder B when filled with air. As soon as the water has come to rest, the time of effusion of the volume of air between the marks *m* and *n* is determined. (According to Pannertz, bands of fine card round the marks permit of greater accuracy of observation.) The stopcock on *b* is first turned so as to communicate with the head *c*; the level of the water in the lower part of the cylinder B then begins to rise, displacing the air, and the time is taken with a stop-watch as soon as the meniscus passes the mark *m*; another reading is taken when the meniscus of water passes *n*, and the time between the two readings is noted. The residual air in B is then displaced by the gas to be examined by connecting stopcock *a* with the supply, and opening *b*; the gas is allowed to pass through for about two minutes. The displacement of the air is accelerated by slowly raising B almost completely out of the water and lowering it again. The outlet of *b* is then closed, B is again raised to fill it completely with gas, the inlet of *a* closed, and B again placed in position. After the water has come to rest, the time of effusion of the gas is measured under exactly the same conditions as with the air so that the time of effusion of equal volumes of air and gas, contained between *m* and *n* is ascertained. The calculation of the specific gravity is then made by the formula given above.

As the air and gas are both measured in a state saturated with moisture and at the temperature of the water by which they are confined, all corrections with respect to vapour tension and temperature are obviated. It is well, however, to read the temperature by the thermometer *t* before and after the experiment, as a check. For exact work the test should be repeated; the times observed in the duplicate tests should not differ from each other by more than 0·2 second.

The following is an example of the determination of the specific gravity of coal-gas :—

$$\text{Time of effusion observed for gas} = 2'\ 25.1'' = 145.1''$$
$$\text{,, \quad ,, \quad air} = 3'\ 40.8'' = 220.8''$$
$$\text{Specific gravity} = \frac{145.1^2}{220.8^2} = 0.4321.$$

In order to avoid this rather troublesome calculation, Krug, at the suggestion of Pfeiffer (*J. Gasbeleucht.*, 1903, p. 451), has drawn up a table of co-ordinates which permits a direct reading of the specific gravity from the times of effusion (obtainable rom Messrs Oldenbourg of Munich).

The results obtained with Schilling's apparatus are reliable to the third decimal place, and this method is always to be preferred when accuracy is important, as, for example, in the calculation of the calorific value from the analysis.

A "specific-gravity bell," depending on the same principle as the above apparatus, is made by Messrs A. Wright & Co., Westminster. Other apparatus on the same principle are described by Gülich (*J. Gasbeleucht.*, 1911, p. 699); Felix Meyer (Ger. P. appl. M, 47821; *Z. angew. Chem.*, 1913, p. 121); A. R. Myhill (*Gas World*, lviii. p. 763).

An apparatus for estimating the density of gases on the principle employed by Bunsen and Schilling, used in the laboratory of the Karlsruhe Technical Laboratory, is described by Hofsäss in *J. Gasbeleucht.*, 1913, p. 871; *Chem. Zentralb.* 1913, ii. p. 4353; *J. Chem. Soc. Abstr.*, 1913, ii. p. 1026. The same apparatus can also be utilised for testing the *viscosity* (internal friction) of the gas. It is sold by C. Desaga of Heidelberg.

(c) *The Gas-Balance of Lux.*

This apparatus, described in *J. Gasbeleucht.*, 1887, p. 251, is very much employed in the daily practice of gas-works, as it indicates the specific gravity of the gas directly. It depends upon the simple principle of directly weighing equal volumes of air and gas, the difference of which in weight is shown as specific gravity (air = 1) by the displacement on a scale. The globe-shaped receiver, Fig. 85, which may be made of glass, balances with the beam on two steel points s s_1, Fig. 84, which move in a hollow, conical steel groove. The fork-shaped end of the pillar carries the gas inlet r and outlet o, which communicate with the small cups p and p_1, which are filled with mercury. Two small tubes are attached to the beam of the balance at right angles to the plane of swing, the ends of which are bent at right angles and are connected with the inlet and outlet of the pillar by the mercury seal of the cups p and p_1, without interfering with the movement of the beam. One of the small tubes conducts the gas into the globe through a central tube, whilst the other serves as the exit-tube.

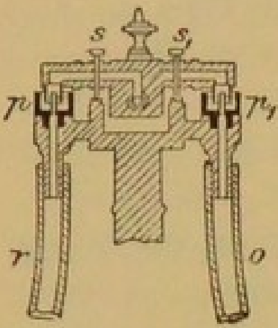


FIG. 84.

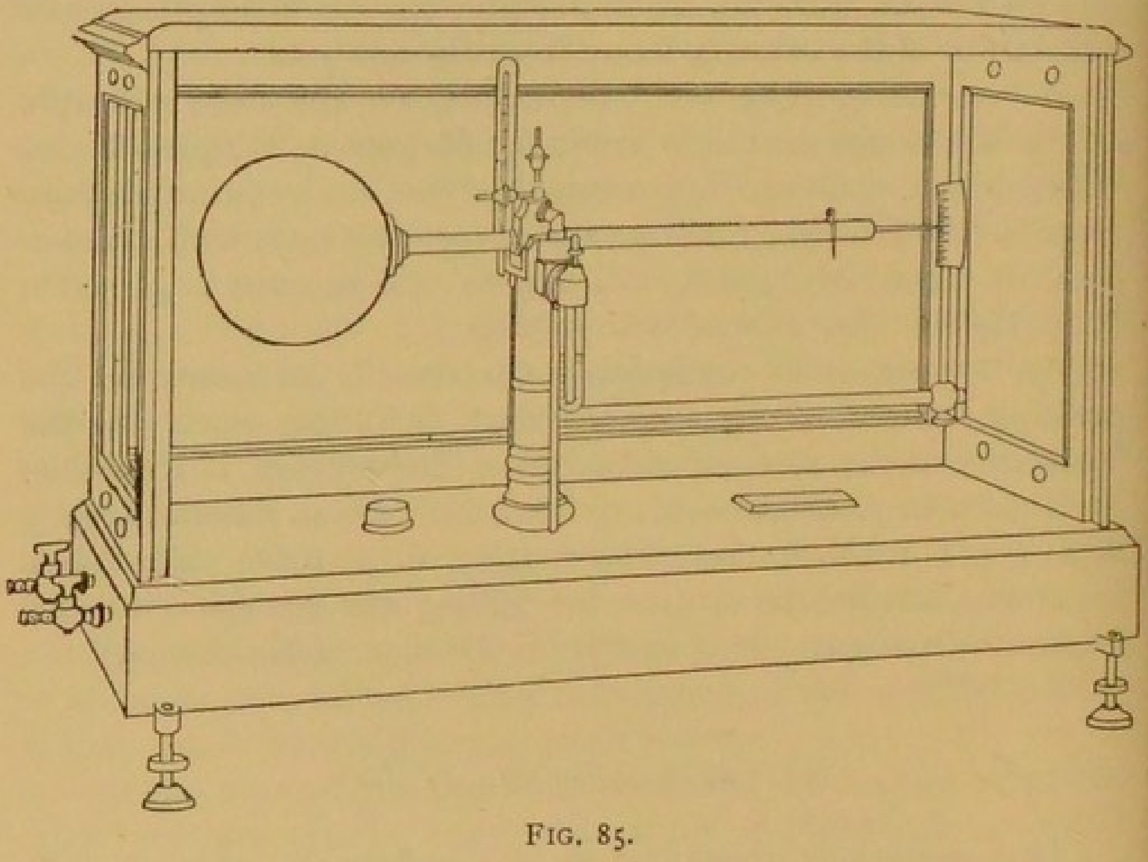


FIG. 85.

The balance is mounted in a glass case provided with a door. The gas inlet and outlet to r and o are connected by two small tubes, each fitted with a stopcock and rubber connection on one of the ends of the balance case. The beam of the balance is divided into 100 divisions, and from each 10 to the next, reckoned from the pivot, there are graduations, 0·0, 0·1, 0·2, . . . 1·0; the beam carries a nickel rider. The graduated air is divided into 50 parts, the middle of which is the zero; the graduations, 0·1, 0·2, etc., are placed above and below from each 10 to the next; the marks below zero are negative values.

The balance must be fixed in a position which is not subject to vibrations, nor exposed to direct sunlight or other sudden changes of temperature. When at rest, the beam of the balance rests firmly on the pillar; it is released by means of a screw at the right-hand end of the case. When the globe is filled with air and the rider is on the outermost mark 1, the pointer should come to rest exactly on the zero mark.

The adjustment of the balance beam is effected by means of a small screw above the middle of the beam, which can be moved horizontally; for further adjustment, the rider is placed on the division 0·8. If the balance has the right sensitiveness, each degree on the graduated arc should correspond to each degree on the beam; the pointer ought then to come to rest at + 0·2 on the arc. This adjustment is made by means of the small screw, which can be moved vertically over the middle of the beam.

In order to ascertain the specific gravity of the gas to be tested, the arc is first displaced from the balance by passing the gas through for five minutes. The rider is then placed on that point of the graduation which is regarded as likely to be nearest to the specific gravity of the gas, for example, 0·4; the beam is then released and the division on the graduated arc on which the pointer comes to rest after swinging up and down is read. This reading added to or subtracted from that of the rider gives the second decimal for the specific gravity; the reading −0·01 would, for instance, indicate a specific gravity of 0·40 − 0·01 = 0·39. The third decimal place can be estimated by the eye; a greater degree of accuracy in the determination is not to be expected.

A table of corrections for barometric pressure and temperature is provided for the apparatus, which influences the results to the fourth place of decimals. A correction of this kind is theoretically necessary on account of the nature of the balance. If, for example, the atmospheric pressure increases, the gas in the globe of the balance as well as the surrounding air is contracted, so that the weight of the contents of the globe, and that of the air displaced thereby, both increase; accordingly the globe of the balance tends to become heavier by the increasing weight of the gas, and lighter in proportion to the greater upward push of the air. The absolute increase in weight is greater in the case of air than in that of gas, in proportion to the difference in their specific gravities; therefore the globe containing the gas becomes relatively lighter with an increase in pressure, and heavier with a decrease in pressure. The necessary correction for the influence of changes of pressure is to add 0·0007 mm. of pressure over 760 mm., and to subtract 0·002 for every degree above 15°, and *vice versa.*

For example, the specific gravity of a gas was found by the balance to be +0·41 at 28° and 775 mm. pressure:

775 − 760 = 15; +0·0007 × 15 . .	+0·0105
28 − 15 = 13; −0·002 × 13 . .	−0·0260
	−0·0155
Corrected sp. gr. 0·41 − 0·0155 . .	0·3945

A table supplied with the apparatus gives the corrections from 0° to 30° C., and from 730 to 790 mm.; it is, however, applicable only to gases of a sp. gr. between 0·4 and 0·5.

For rapid tests following closely upon each other, the apparatus gives satisfactory results to the second decimal place; after any considerable interval, however, say from one day to another, a new adjustment will be necessary, as a rule, on account of the unequal expansion of the dissimilar arms of the beam with changes of temperature, for which no compensation is provided.

The apparatus described by Chandler (*J. Gas Lighting*, cxvii. p. 26) is essentially a Lux gas-balance. On the same principle Arndt's "Econometer" is constructed.

(d) *Other Apparatus for determining the Specific Gravity of Gases.*

Krell (*J. Gasbeleucht.*, 1899, p. 212) has devised an apparatus for determining the specific gravity of gases by measuring, with a delicate differential pressure gauge, the difference between the statical pressure of a long vertical column of gas and a column of air of equal length.

Threlfall (*Proc. Roy. Soc.*, A., 1906, p. 542; *J. Soc. Chem. Ind.*, 1897, p. 359) has indicated an apparatus on the same principle.

Other apparatus have been devised by Pannertz (*J. Gasbeleucht.*, 1905, p. 901); Knoll (Ger. P. 247738); Simmance and Abady (B. P. 27484 of 1911; Ger. P. 266538); Dosch (Ger. P. 242704); Shaffner (Amer. P. 1065974); G. E. Wolf (Fr. P. 456295 and Ger. P. 268352; *Z. angew. Chem.*, 1904, ii. p. 10); Kalähne (Ger. P. 268353); Burkhardt (Ger. Ps. 262867 and 266679); Contzen ("Hydro"-Apparatus sold by J. von Geldern & Co., Düsseldorff); Hofsäss (*J. Gasbeleucht.*, 1913, lvi. p. 841); Aston (*Proc. Roy. Soc.*, 1914, p. 439); Bomhard and König (Ger. P. 269862).

Estimation of the Specific Gravity of Gases in Motion.—Fel. Meyer (Ger. P. 258858) drives the gas to be examined, mixed with a gas of known composition, or else the latter mixed with the former, through measuring-apparatus gauged for the density of the gas, by which the velocity of the current or the quantity of the gas is measured, and the specific gravity of the gas is read off. He calls this instrument "Rotameter." Preferably two similar measuring devices connected by a long tube are used. The whole is filled with the gas under examination, and a gas, *e.g.* air of known specific gravity, is passed into the first measuring device, thus causing an equal quantity of the gas under examination to pass through the second measuring device. In this way the first measuring device indicates the velocity of the known gas, and hence also of the gas under examination, whilst the specific gravity of the latter can be ascertained from the indication of the second measuring device.

Dosch (Ger. P. 242704) places within a case containing the gas and closed (except the pipes for the entrance and the exit of the gas) a revolving wheel (a "flying pinion"), and, at different distances from the axis of the latter, two pipes leading to one or two differential pressure gauges, thus utilising the statical or the velocity pressure for estimating the specific gravity of the gas. Special openings in the entrance and exit pipes permit of altering the difference of pressure at the same time of revolutions of the wheel, and increasing the exactness of the indications with the same pressure gauge. On the axis of the wheel another equal wheel may be fixed, which turns within a case filled with a gas serving for comparison, thus doing away with the necessity of a special counter for the number of revolutions. This apparatus may be used for the continuous estimation of hydrogen in producer-gases.

Chabaud, in his Ger. P. 264714, describes an apparatus for the continuous indication of the specific gravity of gases in motion by means of a float, which is kept in suspension by the gases, and which admits of reading the specific gravity at a graduated pipe without any manipulation.

VII. Measurement of Pressure and of Draught.

For the technical analysis of gases, in many cases the pressure of a current of gas must be determined, apart from the necessity of observing such pressures for properly carrying out manufacturing processes. This subject is treated in detail in Lunge's *Technical Methods of Chemical Analysis*, translated by C. A. Keane, vol. i. pp. 165 *et seq.* (1908); in this place we shall merely give an outline of it.

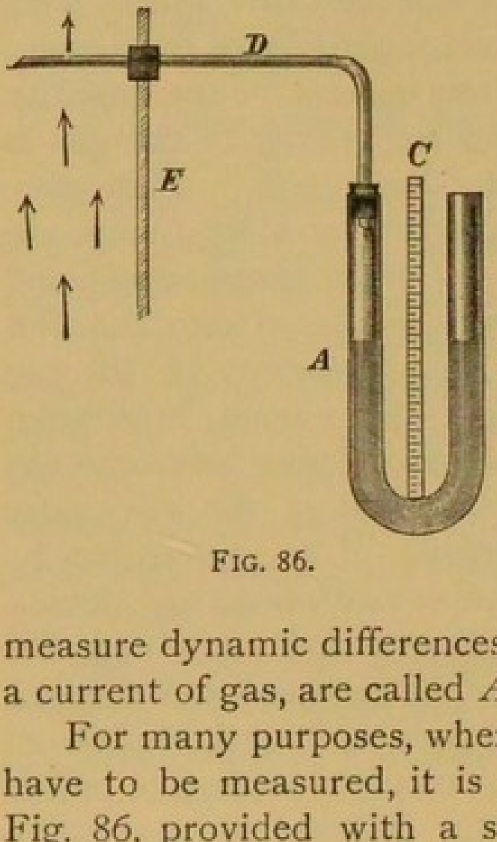


Fig. 86.

Instruments which measure the statical difference of pressure, say, between the inside of an apparatus and the outer atmosphere, are called *Pressure Gauges* or *Manometers*. Those which measure dynamic differences, registering directly the velocity of a current of gas, are called *Anemometers*.

For many purposes, where only small differences of pressure have to be measured, it is sufficient to employ U-tubes A, B, Fig. 86, provided with a scale C. The limb A is connected with the tube D, which passes through the wall E of the apparatus in which the gas is contained; the other limb B is open to the outside air. If the pressure within the apparatus is greater than that of the outside air, the liquid will stand at a higher level in B than in A, and inversely. A pressure of

0·1 mm. of water corresponds to a velocity of the gas of 11·23 metres per second.

Such small differences of pressure are more accurately measured by Péclet's pressure gauge shown in Fig. 87. It consists of a bottle A, with a neck near the bottom which is connected with the slightly inclined tube B, 2 or 3 mm. wide, provided with a scale. B is fixed to a vertical board, provided with a spirit level. The liquid, either water or preferably alcohol, forms a very long meniscus in B. If B has an inclination of 1 in 25, each millimetre on this tube represents a difference of pressure of $\frac{1}{25}$ mm. in A. If the scale on B can be read to 0·5 mm., differences of 0·2 in pressure can be measured. The upper portion of the inner walls of the tube B should be moistened before each test by inclining the instrument. Alcohol is preferable to water, both on account of its smaller coefficient of friction, and because it returns more quickly to its original position; but the pressures must then be corrected according to the specific gravity of the alcohol. If this is = 0·800, 1 mm. corresponds to 0·8 mm. of water pressure.

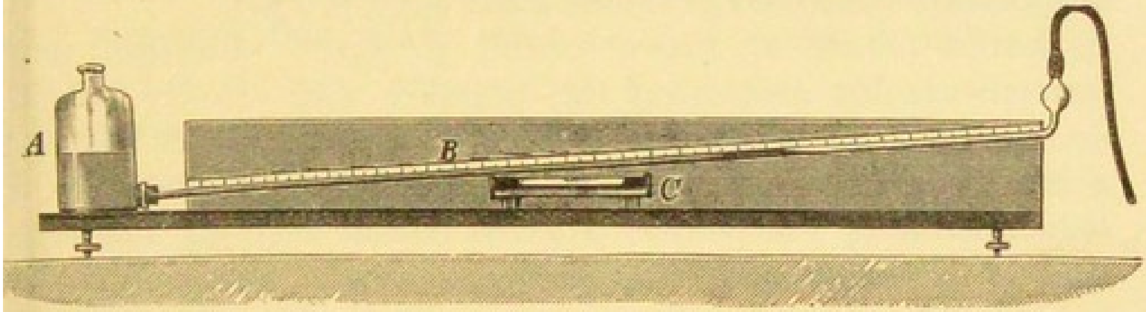


FIG. 87.

Differential manometers are those where two non-miscible liquids are employed in U-tubes or similar apparatus. To this class belong the instruments designed by Seger (described in Lunge-Keane, i. p. 167) and König (*ibid.*, p. 168). Langen's manometer (*ibid.*, p. 169) employs a combination of two tubes of unequal diameter.

In the same place (pp. 169 *et seq.*) the method of calculating the velocity of a current of gas from the manometric pressure by Péclet's formula is explained, and Fletcher's anemometer, modified by Lunge, is described, which utilises this method for practical purposes. There also tables are given for reducing the anemometer readings to velocity of current expressed in feet or metres per second.

An apparatus for determining the composition and velocity of gas mixtures is described in W. Heckmann's Ger. Ps. 252538 and 259600. The gas is led into a throttle chamber connected with a differential pressure gauge, and an absorbing liquid is sprayed into the chamber, or contained in a separate vessel, so that the pressure gauge registers not only the pressure corresponding to the velocity of the gas mixture, but also the diminution of pressure caused by the absorption of one of the constituents.

Verbeck's "Precision-differential manometer" and "Precision-control-manometer" for testing the draught and velocity of gases are described in *Chem. Zeit.*, 1913, p. 1361.

Lütke (*Stahl u. Eisen*, xxxiii. p. 1307) describes new instruments for measuring the pressure and velocity of gas and steam. The apparatus consists of a long pointer pivoted a short distance from one end. On one side of the pivot is suspended from the pointer a small bucket carrying mercury, and on the other side is suspended a weight which serves to balance the pointer in a horizontal position. Into the mercury bucket dips one end of an inverted U-tube, the other end of which is connected with the bottom of the receiver. The tube acts as a syphon, and under normal conditions the pointer is balanced with the mercury in both receiver and bucket at the same level. Through the sealed top of the receiver a tube passes to the pipe in which the pressure is to be measured. The pressure or suction in the pipe forces mercury from the receiver into the bucket, or *vice versa*, thus causing the pointer to move up or down. With proper calibration the instrument thus makes a direct record. For measuring a difference in pressure, it is necessary to have two sets of mercury buckets and receivers.

VIII. Determination of the Calorific Value of Gases.

The calorific power of gaseous mixtures is of extreme importance for their technical uses. This holds good, not merely of gaseous mixtures intended from the outset for heating purposes, such as producer-gas, water-gas, etc., but nowadays also for coal-gas (illuminating gas), not merely on account of its use for heating domestic stoves, etc., but even n connection with its illuminating properties (which are not treated in this book, but for which we refer the reader to the article on "Illuminating-Gas and Ammonia," in vol. ii. of Lunge's *Technical Methods of Chemical Analysis*, translated by Keane, vol. ii. pp. 697 *et seq.*), since the Auer-Welsbach process and other processes for incandescent burners have spread all over. It is estimated that in Great Britain not more than 10 per cent. of the gas for illuminating purposes is now burned in open flames, and on the Continent the proportion is still smaller.

Whilst the illuminating power of a gas is not an absolute quality of it, but varies greatly with the construction of the burner employed, the rate at which the gas is burned, etc., etc., and therefore this power must be determined under certain specified conditions, varying very greatly at different works, the calorific power is an absolute quality of the gas, representing its total potential energy, expressed in heat-units. Provided that the combustion is complete, the calorific power remains the same whatever burner is employed, and whatever the rate of combustion.

The *unit of heat* employed for calorific determinations in Great Britain is the British Thermal Unit (usually denoted B. Th. U., to distinguish it from the electrical Board of Trade Unit, for which the contraction B. T. U. is employed), and is the quantity of heat required for raising 1 lb. of water 1° F. The calorific power of a gas is usually stated in the number of B. Th. U., evolved in the combustion of 1 cb. ft. of the gas. On the Continent, the heat unit employed is the larger caloric (Cal.) and the results are stated in calories per cubic metre. The calorific power tests of London gas, carried out under the instruction of the Metropolitan Gas Referees, are recorded in calories per cubic feet.

For conversion of metrical calories into B. Th. U., the factor is 3·968; that for converting calories per cubic metre into B. Th. U. per cubic foot is 0·1124.

In the determination of the calorific power of gases containing hydrogen, the steam produced by the combustion is condensed to liquid water in the calorimeter, and the latent heat of such steam is therefore always included in the observed calorific power, which is called the *Gross Calorific Power*. This latent heat can, however, be utilised in practice only in the very exceptional cases where the products of combustion are completely cooled to atmospheric temperature. It is, of course, never evolved in the flame itself, and takes no part in the development of the flame temperature; nor is it evolved in the cylinder of a gas-engine, and is therefore unavailable for the production of mechanical energy. As the latent heat of steam is known = 0·537 cal. or 2·13 B. Th. U. for each cubic centimetre or gramme of the water condensed, this latent heat can be ascertained by collecting and measuring the amount of water obtained during the test. The deduction of this amount from the gross value gives the *Net Calorific Power*.

As the results are stated per unit volume of the gas, it is necessary to define the *standard temperature and pressure* at which the gas is measured. In Great Britain the standard conditions are: that the gas shall be measured in the moist state, at 60° F. and 30 in. pressure. A table for obtaining the volume of a gas under these conditions, from its volume at temperatures of from 40° to 80° F., and from 28·0 to 31 in. pressure, is given in Lunge-Keane's book, ii. pp. 690-691. In Germany, the results are sometimes stated for dry gas at 0° C., and sometimes for moist gas at 15° C. and 760 mm. The latter conditions are practically identical with the British conditions of moist gas at 60° F. and 30 in., and considerable confusion is often caused thereby, when the standard conditions are not specified.

Abady (*J. Gas Lighting*, cxx. p. 956) points out that, along with determining the heating value of coal-gas, etc., the *specific gravity* of the gas should be regularly determined, since in this manner the fluctuations of the former can be more easily explained. As a rule the heating value rises in the same ratio as the specific gravity; still, cases occur where the specific gravity goes up, while the heating value goes down. This proves that either the percentage of carbon dioxide, or that of the nitrogen, or both, are increasing, and corresponding measures must be taken, whereas the mere determination of the heating value does not indicate this. The same author later on (*ibid.*, cxxi. p. 527) recommends for the examination of illuminating gas, Simmance's "total-heat calorimeter," which works with dried combustion air, and is therefore independent of the variations of moisture in atmospheric air.

Calculation of the Calorific Value of Gaseous Mixtures from the Analysis.

For this purpose we must start from the scientifically determined calorific values of the single constituents of the gaseous mixture. In the following table (IX.—A, p. 194) (from Lunge-Keane, vol. ii. p. 693) the gross and net calorific values of a number of gases are given of unit volume of the constituents present in any quantity in ordinary coal-gas, both in Cal. per cubic metre, and B. Th. U. per cubic foot. Further, in each set, figures are given for showing the values at (*a*) 0° C. and 760 mm., or 32° F. and 30 in. dry; (*b*) 15° C. and 760 mm., or 60° F. and 30 in. dry; and (*c*) 15° C. and 760 mm., or 60° F. and 30 in. moist. The figures in the table are calculated from the observed calorific power of known weights of the various gases and their specific gravities, Thomsen's values being employed except in the case of benzene vapour. The figures found for the latter by Thomsen, Berthelot, and Stohmann vary considerably, and as the latter approximates to the average of all the values obtained, it has been taken in preference to Thomsen's figure.

The figures given for the *net* values in the table are obtained by deducting the latent heat of the steam produced (0·537 cal. per cubic centimetre) from the gross figures. In calorimetric tests t is usual to deduct roundly 0·6 cal. for each cubic centimetre of condensed water, which includes the latent heat of the steam, and also approximately the sensible heat evolved in the calorimeter by the cooling of the condensed water from 100° C. to ordinary emperature. This last amount should, however, not be deducted, if the net thermodynamic value is to be ascertained as it is evolved as heat in the flame, and contributes to the development of flame temperature and of mechanical energy under normal conditions. An additional table (IX.—B) is given, showing the further deductions which must be made from the net values given in the first table, if it be desired to allow also or the sensible heat of the condensed steam.

From the value of the constituents given in the table, the

IX.—A. *Calorific Power of Gases on Combustion.*

	Calories per cubic metre.						B. Th. U. per cubic foot.					
	0° C. and 760 mm. Dry.		15° C. and 760 mm. Dry.		15° C. and 760 mm. Moist.		32° F. and 30 in. Dry.		60° F. and 30 in. Dry.		60° F. and 30 in. Moist.	
	Gross.	Net.	Gross.	Net.	Gross.	Net.	Gross.	Net.	Gross.	Net.	Gross.	Net.
Hydrogen	3,056	2,621	2,897	2,484	2,848	2,443	344	295	326	279	321	275
Carbon monoxide . .	3,056	...	2,897	...	2,848	...	344	...	326	...	321	...
Sulphuretted hydrogen .	6,170	5.745	5,849	5,446	5,751	5,355	693	645	657	612	646	602
Methane	9,572	8,699	9,074	8,246	8,922	8,108	1,076	977	1,020	927	1,003	911
Ethylene	15,063	14,190	14,279	13,451	14,041	13,226	1,692	1,594	1,605	1,511	1,578	1.486
Propylene	22,136	20,832	20,983	19,747	20,633	10,417	2,487	2,341	2,358	2,219	2,319	2,182
Benzene vapour . .	35,397	34,093	33,553	32,318	32,992	31,777	3,977	3,831	3.771	3,631	3,708	3.570

B. *Further Deduction from Net Value to be made, if the Sensible Heat of the Condensed Water evolved by the Cooling from* 100° *to* 15° *C. is to be allowed for.*

	Calories per cubic metre.			B. Th. U. per cubic foot.		
	0° C. and 760 mm. Dry.	15° C. and 760 mm. Dry.	15° C. and 760 mm. Moist.	32° F. and 30 in. Dry.	60° F. and 30 in. Dry.	60° F. and 30 in. Moist.
For H_2 and H_2S . .	68	64·5	63	7·6	7·25	7·1
„ CH_4 and C_2H_4 . .	136	129·0	126	15·2	14·5	14·2
„ C_3H_6 and C_6H_6 . .	204	193·5	189	22·8	21·75	23·1

calorific power of a gaseous mixture may be calculated by multiplying the percentage of each constituent by its calorific power, and dividing the sum of the multiples by 100, as shown in the following example:—

	Per cent. by vol.		Gross cal. power at 60° F. and 30 in. moist.		Multiple.
CO_2 . .	1·2	×	nil	=	...
C_nH_m . .	3·4	×	2,319	=	7,885
O_2 . .	0·3	×	nil	=	...
CO . .	6·8	×	321	=	2,183
CH_4 . .	32·9	×	1,003	=	32,999
H_2 . .	49·2	×	321	=	15,791
N_2 . .	6·2	×	nil	=	...
					58,858 ÷ 100 = 588·6

The calculated calorific power of such a sample of gas is therefore, 588·6 B. Th. U. gross per cubic foot measured moist at 60° F. and 30 in.

The value thus obtained is, of course, subject to all the errors of analysis, and a further possibility of error arises from the uncertainty as to the exact composition of the heavy hydrocarbons, C_nH_m. It is customary to assume that the mixture of these has the same calorific power as propylene, as has been done above, but this can only be regarded as an approximation. Usually, however, in the case of coal-gas, the analyses thus calculated agree to within 2 to 3 per cent. with the figures obtained by the calorimeter. With carburetted water-gas, in which a much higher percentage of unsaturated hydrocarbons is present, the agreement is often much less satisfactory.

If the percentages of ethylene and benzene have been determined separately by any of the methods previously described, these figures are multiplied by their respective calorific powers, instead of employing the propylene values.

The application of the values of the composition of gases by means of gas-analysis to the calculation of their calorific value has been studied experimentally by F. S. Wade (*J. Gas Lighting*, 1912, cxx. p. 518). While the calorific value of ordinary coal-gas can be accurately ascertained from its analysis, in the case of oil-gas the calorific values calculated from its composition is always lower by 7 per cent. than that found in the calorimeter, probably owing to the presence of heavy hydrocarbons of greatly varying composition.

The Direct Measurement of the Calorific Power.

In place of the indirect and tedious estimation of the calorific power by calculation from the complete analysis (which frequently is not available), this value is now nearly always obtained by direct measurement.

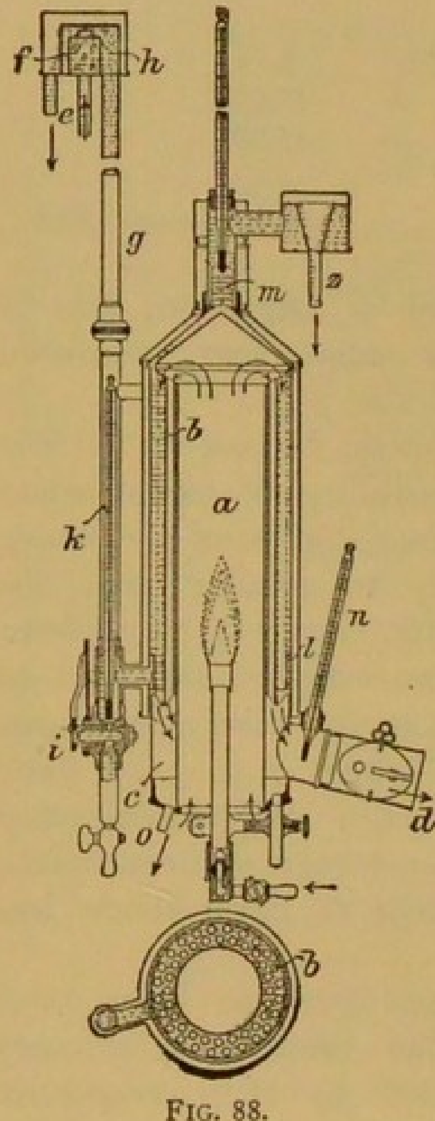


Fig. 88.

The calorimeters in use for estimations, in which large volumes of gas are available, are all modifications of the calorimeter devised by Hartley in 1882 (*J. Gas Lighting*, 1884, p. 1142), in which the gas is burned at a constant rate in a chamber through which water is also flowing at a constant rate. From the volume of the gas consumed and of water passed in a given time through the apparatus, and the average increase in the temperature of the water, the calorific power is readily calculated. The amount of water condensed from a given volume of gas also supplies a ready means of ascertaining the necessary deduction for the latent heat of water required to determine the net calorific power.

(a) *Junckers' Gas Calorimeter.*—In this apparatus, the heat generated by the flame of burning gas is transmitted to a current of water flowing at a constant rate, and measurements are made of the volume of gas burnt, the quantity of water heated, the difference in temperature of the water on entering and leaving the apparatus, and the quantity of water condensed from the products of the combustion. The gas is burnt in a large Bunsen burner (Fig. 88) in the combustion chamber *a*, which consists of an annular copper vessel, the annular space being traversed by a number of upper tubes *b*, connecting the top with the bottom of the chamber. The products of combustion pass through these tubes in a downward direction, the condensed water being collected at *o*, and the waste gases escaping through the side-tube *d*. The current of water enters at *e*, where it passes through a sieve *h*, and enters the calorimeter through *g* and *i*, thus circulating in an opposite direction to that of the products of combustion, whereby complete cooling of the latter to the temperature of the water is effected. The water, after passing through the annular chamber, goes over a series of baffle plates at *m*, to ensure thorough mixing, and then passes out though the overflow *z*, where it is collected and measured. The pressure of water is kept constant by the two overflows at *h* and *z*, the water being run into *h* at a greater rate than it passes through the calorimeter; the rate of flow is regulated by the cock *i*. The temperature of the entering water is taken by the thermometer *k*, that of the exit water by the thermometer above *m*. The whole instrument is enclosed in a cylindrical air-jacket of polished or plated copper to prevent radiation.

The whole apparatus, as arranged for actual experiment, is shown in Fig. 89. The gas to be tested is measured in a small wet meter, provided with a thermometer, and is passed through a governor to ensure a steady pressure of gas at the burner; a water-pressure gauge is attached to the governor, which indicates the pressure, above that of the atmosphere, at which the gas is measured. As the water supply may vary considerably in temperature, even within a short period of time, if taken directly from a tap, it is preferable to have a large reservoir for its storage. Pfeiffer recommends a sheet-zinc tank of 60 litres capacity (H, Fig. 89), provided with a pipe *w*, which serves both for filling and discharging, a glass gauge and an overflow pipe *u*; the pipe *w* is connected with the pressure box of the calorimeter through the tap *v*. The experiment should be so regulated that the temperature of the exit gases at *s* (Fig. 89) is the same as that of the laboratory, so that they are only saturated with the quantity of moisture corresponding to this temperature. Instead of measuring the water collected from *c*, Pfeiffer prefers weighing it in the bottle F, of about 10 litres capacity, the weight of the empty bottle having been previously determined.

The condensed water from the calorimeter is collected in the measuring cylinder *d* (Fig. 89), which is placed in position after the gas-meter index has completed a revolution, from the start of the experiment, and the collecting continued for a corresponding period after the bottle F has been removed.

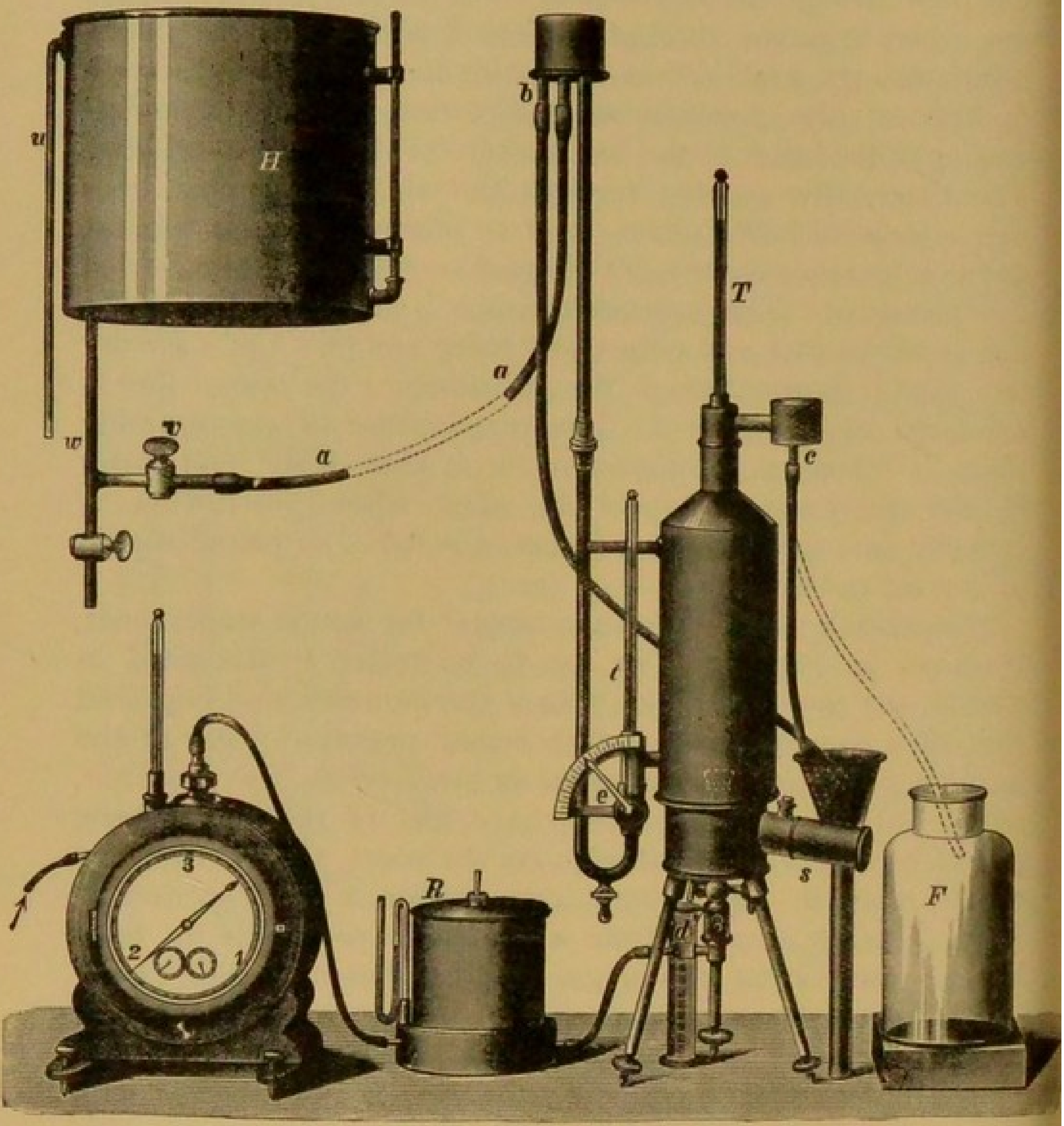


FIG. 89.

To carry out a test, the water is first turned on, and when it is running from both overflows, the gas is lighted and the speed of the water regulated by the cock *i*, so that there is a difference of from 10° to 20° between the inlet and outlet thermometers. Illuminating gas is burned at the rate of from 100 to 300 litres (4 to 11 cb. ft.) per hour, hydrogen-gas from 200 to 600 litres, producer-gas at the rate of from 400 to 1000 litres (14 to 35 cb. ft.). When the difference in temperature of the two thermometers is nearly constant, and the condensed water is dripping regularly into *d*, the test can be begun. This is done by waiting until the gas-meter index passes any desired point, and then quickly introducing the outlet water tube *c* into a suitable measuring vessel; a series of readings of the thermometer are taken whilst about 28 litres (1 cb. ft.) of gas is burnt, and the volume of gas and of collected water measured. The inlet thermometer *k* should be read every minute, and the outlet thermometer T (Fig. 89) every half minute.

The calorific value is:

$$\frac{\text{Weight of water} \times \text{temperature difference}}{\text{Volume of gas consumed}},$$

the volume of gas being corrected for temperature and pressure.

The value thus obtained represents the calorific power of the gas, when the water formed by the combustion is converted into the liquid state in the calorimeter. To obtain the calorific value when the water formed escapes as steam, the latent heat of the condensed water must be deducted; the quantity of heat evolved by each cubic centimetre of condensed water may be taken, with sufficient accuracy for most purposes, =0·6 cal. (1 cal.=the amount of heat required to raise 1000 g. of water 1° C.), and this value, multiplied by the number of cubic centimetres of water condensed and divided by the gas consumed, will give the total heat to be deducted from the "gross" calorific value to give the "net" calorific value of the gas, with the water formed in the combustion remaining as steam. The result in calories, multiplied by 3·97, gives the calorific value in British thermal units.

No further corrections are necessary, and the results are in every respect satisfactory, if the experimental conditions are properly carried out. It is important that the determinations should be made in a room free from any considerable variation of temperature.

If a larger flame is used, the combustion is apt to be incomplete; F. Fischer accordingly recommends ascertaining by a preliminary experiment that the waste gases contain several per cent. of oxygen, as otherwise the result may be 5 per cent. or more too low.

Example:

Volume of gas consumed (5 revolutions of meter index, at 3·06 litres per revolution)	15·3 litres
Weight of water	5310 g.
Temperature of inlet water, constant	13·8°
„ outlet water, 28·1, 28·15, 28·15, 28·1, 28·1, 28·1, 28·1, 28·1	mean 28·11°
Difference of temperature	14·31°
Volume of condensed water	14 c.c.
Temperature of room	22°
Barometer	766 mm.
Gross calorific value per cubic metre, at 15° C and 760 mm. $= \frac{5{\cdot}310 \times 14{\cdot}31}{0{\cdot}0153} \times \frac{273+22}{288} \times \frac{760}{766}$	5082
Net calorific value per cubic metre, at 15° C and 760 mm. $= \frac{(5{\cdot}310 \times 14{\cdot}31) - 0{\cdot}6 \times 14}{0{\cdot}0153} \times \frac{273+22}{288} \times \frac{760}{766}$ . .	4533

Pfeiffer (*J. Gasbeleucht.*, 1904, p. 684) regards the above method of calculating the net calorific value as somewhat inaccurate, on account of the small quantity of condensed water collected in a single experiment. As the result of his own observations, he is of opinion that it is best calculated from the gross calorific value on the basis of independent experiments in which 50 to 70 c.c. condensed water are collected. From numerous determinations he finds that the net value is 11·1 per cent. less than the gross value in the case of gas made from English or from Westphalian coal, and, as an average, 8·6 per cent. less in the case of carburetted water-gas. From these data, the net calorific value may be calculated directly from the experimental determination, without reference to the volume of condensed water formed. To facilitate the correction, Pfeiffer has constructed a table, which is reproduced in Lunge-Keane's *Technical Methods*, vol. ii. p. 231.

Junkers supplies to the buyers of his calorimeter a table for estimating the heating values by it.

An extensive study of the Junkers calorimeter has been made by Immenkötter in his booklet "Ueber Heizwertbestimmungew mit besonderer Berücksichtigung gasfömiger Breunstoffe," published by Oldenbourg, Munich, an abstract of which is given in *J. Gasbeleucht.*, 1905, p. 736.

Junkers has also modified his calorimeter so as to become an *automatically registering apparatus* (Ger. Ps. 174753 and 190827; *J. Gasbeleucht.*, 1907, p. 520). He effects this by keeping the relation between the quantities of gas and water constant, so that the difference of temperature is a direct measure of the heating value, being proportional to it. The difference of temperature between the inflowing and outflowing water is measured by a thermo-element, and the indications of the voltmeter showing the tension are continuously registered on a strip. A registering gas-calorimeter is also described by Fahrenheim (*J. Gasbeleucht.*, 1907, p. 1019).

Coste and James (*J. Soc. Chem. Ind.*, 1911, p. 67) object to the Junkers gas-calorimeter that the water used in it may be heated by the air of the room. To avoid this, they correct the test by a blind test, or they preheat the water to the temperature of the laboratory.

Bücher (*Z. Verein. deutsch. Ingen.*, 1911, p. 1110) found in the exit gases some unburnt methane, causing a loss of 1 or 2 per cent. of the heating value. In spite of this he considers the Junkers calorimeter as a sufficiently correct instrument for practical purposes.

Allner (*Gas Age*, xxxii. p. 15; *J. Gasbeleucht.*, 1913, lvi. p. 489) describes a contrivance for starting an alarm bell in case of a sudden stoppage of the gas or water supply in the registering-calorimeter of Junkers.

(b) *Boys' Gas-Calorimeter* (*Proc. Roy. Soc.*, 1906, series A, p. 122. The apparatus is made by J. J. Griffin & Sons, Kingsway, London).—This apparatus is prescribed by the Metropolitan Gas Referees (1906) for testing the calorific value of illuminating gas. It has been designed with the object of providing ample space for the circulation of the stream of gases, so that they pass slowly and freely through the instrument, and are thus effectively exposed to the cooling surfaces. The water content of the instrument is reduced to the smallest quantity, so that the outflowing water attains its ultimate temperature very quickly after the gas is lighted. The whole of the circulating water takes the same course continously, being debarred from any parallel or alternative routes, and thus unequal heating and the attendant irregularity of the temperature at the outflow are avoided. The small content of water suffices to abstract the whole of the heat from the slowly travelling stream of gases, owing partly to the avoidance of parallel routes, but mainly by reason of its flow through a pipe of small diameter, the heat-collecting power of which is greatly increased by attached wires.

This calorimeter is shown in vertical section, one-half natural size, in Fig. 90. It consists of three parts which may be separated, or which, if in position, may be turned relatively to one another about their common axis. The parts are (1) the base R, carrying a pair of burners B, and a regulating tap. The upper surface of the base is covered with a bright metal plate, held in place by three centring and lifting blocks C. The blocks are so placed as to carry (2) the vessel D, which is provided with a central copper chimney E, and a condensed water outlet F. Resting upon the vessel D are (3) the essential parts of the calorimeter, attached to the lid G. At the centre where the outflow is situated there is a brass box, which acts as a temperature-equalising chamber for the outlet water. Two dished plates of thin brass, K, are held in place by three scrolls of thin brass, L L L. The lower or pendent part of the box is kept cool by water, circulating through a tube which is sweated on to the outside of the bell. Connected to the water-channel at the lowest point by a union, are six turns of copper pipe, such as is used in a motor-car radiator of the kind known as Clarkson's. In this, a helix of copper wire threaded with copper wire is wound round the tube, and the whole is sweated together by immersion in a bath of melted solder. A second coil of pipe of similar construction, surrounding the first, is fastened to it at the lower end by a union. This terminates at the upper end in a block, to which the inlet water-box and thermometer-holder are secured by a union, as shown at O. An outlet water-box P and thermometer-holder are similarly secured above the equalising chamber. The lowest turns of the

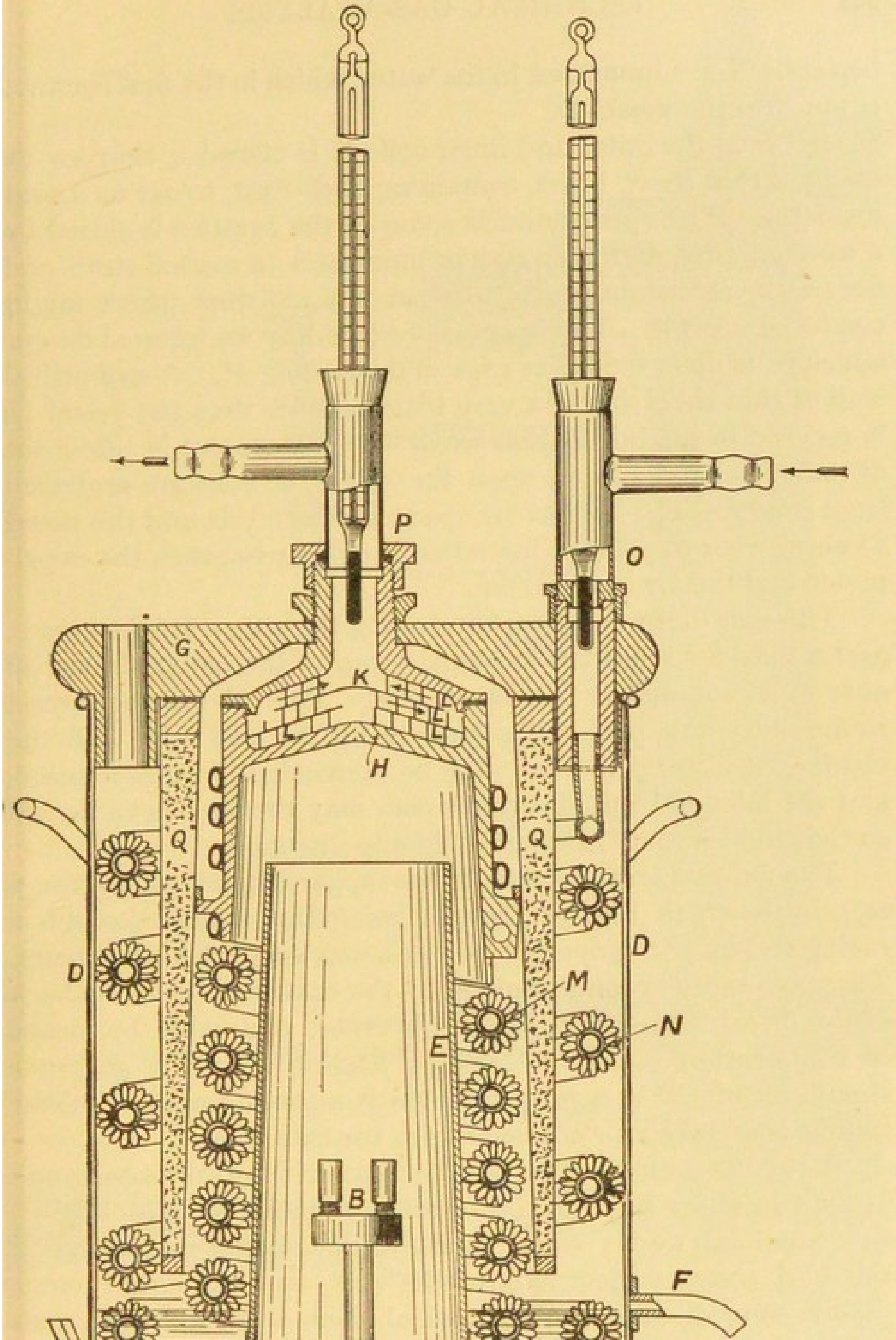


FIG. 90.

two coils N are immersed in the water, which in the first instance is put into the vessel D.

Between the outer and inner coils N is placed a brattice O, made of thin sheet brass, containing cork dust, to act as a heat insulator. The upper annular space in the brattice is closed by a wooden ring, and this end is immersed in melted rosin and bees-wax cement, to protect it from any moisture which might condense upon it. The brattice is carried by an internal flange, which rests upon the lower edge of the casting H. A cylindrical wall of thin sheet brass, a very little smaller than the vessel D, is secured to the lid, so that when the instrument is lifted out of the vessel and placed upon the table, the coils are protected from injury. The narrow air space between this and the vessel D also serves to prevent interchange of heat between the calorimeter and the air of the room.

The two thermometers for reading the water temperatures, and a third for reading the temperature of the outlet air, are all near together, and at the same level. The lid may be turned round into any position, relatively to the gas inlet and the condensed water drip, that may be convenient for observation, and the inlet and outlet water-boxes may themselves be turned so that their branch tubes point in any direction.

The general arrangement of the apparatus, as set up for a test, is shown in Fig. 91, the gas being first passed through a meter and balance governor before being led to the calorimeter. The gas supply is connected up to the central tube at the back of the meter and thence to the governor, preferably by means of composition piping. The pipe leading from the governor should terminate in a nozzle, to which a short length of rubber tubing is attached for connecting to the calorimeter.

A regular supply of water is maintained by connecting one of the two outer pipes of the overflow funnel, shown in Fig. 91, to a small tap over a sink. The overflow funnel is fastened to the wall about 1 meter above the sink, and the other outer pipe is connected to a tube, in which there is a diaphragm with a hole 2·3 mm. in diameter. This tube is connected to the inlet-pipe of the calorimeter. A piece of stiff rubber tubing, long enough to carry the overflow water clear of the calorimeter, is slipped on to the outflow branch, and the water is turned on so that a little of it escapes by the middle pipe of the overflow

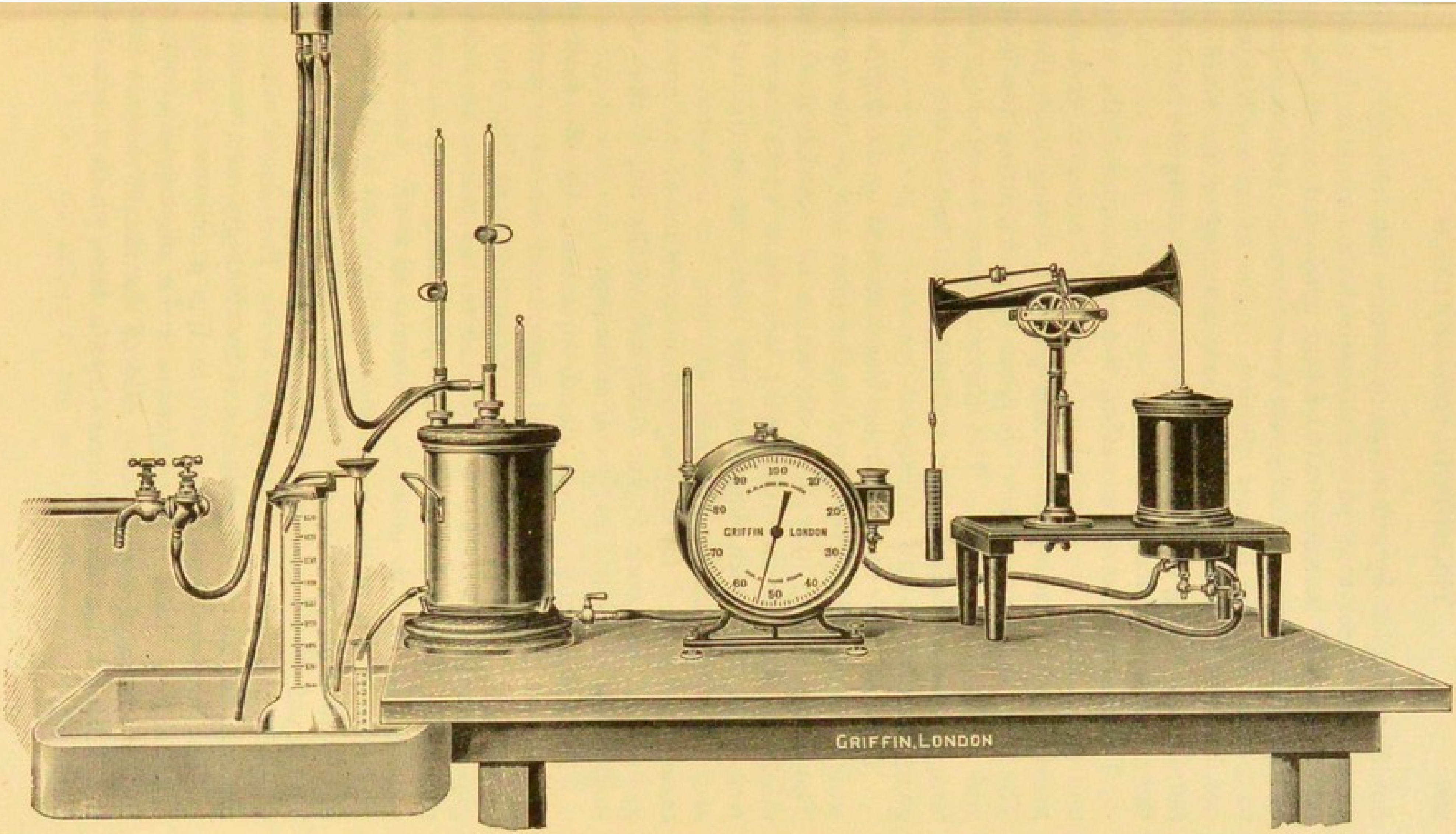


FIG. 91.

funnel, and is led by a third piece of tube into the sink. The amount of water that passes through the calorimeter in four minutes should be sufficient to fill the graduated vessel, shown in Fig. 91, to some point above the lowest division, but insufficient to come above the highest division in five minutes. If this is not found to be the case, a moderate lowering of the overflow funnel or reaming out of the hole in the diaphragm will effect the necessary connection.

The thermometers for reading the temperature of the inlet and outlet water are divided into tenths of a degree, and are provided with reading-lenses and pointers sliding upon them. The thermometers are held in place by corks, fitting the inlet and outlet water-boxes. The thermometers for reading the temperature of the air near the instrument and of the outlet gases are divided into degrees.

The flow of air to the burners is determined by the degree to which the passage is restricted at the inlet and at the outlet. The blocks C (Fig. 91) which determine the restriction of the inlet are made of metal, about 5 mm. thick, while the holes round the lid which determine the restriction at the outlet are five in number and are 16 mm. in diameter. The thermometer used for finding the temperature of the effluent gas is held by a cork in the sixth hole of the lid, so that the bulb is just above the upper coil of the pipe.

The calorimeter should stand on a table by the side of a sink, so that the condensed water and hot-water outlets overhang and deliver into the sink, as shown in Fig. 91. A glass vessel is provided of the size of the vessel D, which should be filled with water, in which sufficient carbonate of soda is dissolved to make it definitely alkaline. The calorimeter, when not in use, is lifted out of the vessel D and placed in the alkaline solution, and left there until it is again required. The liquid should not come within 2 in. of the top of the vessel, when the calorimeter is placed in it. The liquid must be replenished from time to time, and its alkalinity maintained.

The measuring vessel, shown in Fig. 91, carries a change-over funnel, which is placed beneath the short tube attached to the hot-water outlet. One side of the funnel delivers into the sink, and the other delivers into a tube, which directs the water into the vessel.

Full details for carrying out a test are given in the *Modification of the Metropolitan Gas Referees for* 1906 (published by Wyman & Sons, Fetter Lane, London, E.C., price 1s. 6d.); the above description is taken from this notification.

Boys' calorimeter has these advantages over Junkers', that the thermometers for the entering and the exit water are at the same level, that the apparatus can be taken to pieces in a few minutes, and that the water contents are reduced from about 1700 to about 300 c.c.

(c) *F. Fischer's Gas-Calorimeter* (Fig. 92) consists of a wooden vessel B, in which nickel-plated copper vessels A and C are contained. A is suspended from the top of B as shown, and C is fitted into B by the water-tight junction at *v*, which should be greased before use. The detachable cover D is provided with an attachment at *t* for inserting a thermometer, and to carry the stirrer R. The inner vessel C is expanded into three lenticular chambers, each of which contains a sheet of metal *n*, serrated round the edge, the object of which is to promote intimate contact between the products of combustion and the inner surface of the colorimeter. The whole vessel is supported on the feet F. The burner E is supported by the socket *f* and the arm *m*, and is so arranged that it can be readily adjusted into position, by means of the tongue *a* and a pin below *f*. A small inverted cone of nickel gauze is placed in the tube of the burner, to prevent the gas from striking back. Even very small flames burn very quietly here. A cone, preferably of platinum gauze, with the apex upwards, may also be fitted to the top of the burner tube. Air enters at the inclined plate *s*, the direction

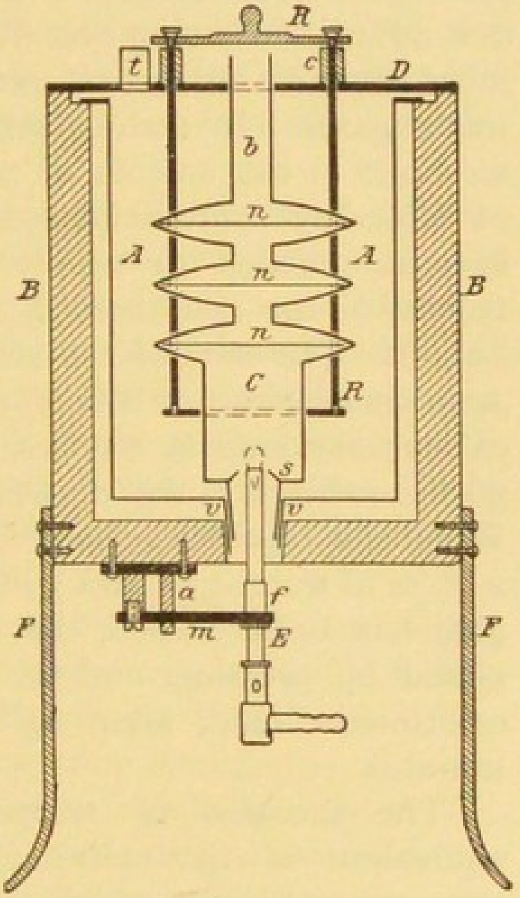


FIG. 92.

of which serves to retain the condensed water in the calorimeter, and the waste gases leave through *b*.

To carry out a determination, the required quantity of water is placed in A, the inner vessel C is placed in position, the cover D put on, and a thermometer inserted at *t*. The water is agitated by the stirrer until the temperature is constant, and the burner drawn down below the body of the calorimeter and attached to the gas supply; the gas should be passed through the meter for some time previous to the determination, in order to saturate the contained water. The burner is then lighted and quickly introduced into the position shown; the flame is adjusted for complete combustion, that adjustment being best determined by a preliminary experiment, so as to ensure an excess of 5 per cent. oxygen in the waste gases. In testing semi-water gas or producer-gas, the air holes at the bottom of the burner are closed; in the case of difficultly combustible gases, such as blast-furnace gas, it is recommended to supply oxygen (about one-fifth of the volume of the gas) through a tube fixed in the centre of the burner. The state of the meter is read off; then *exactly at the same moment* burner B is moved by the right hand beneath the calorimeter until *m* touches *n*, and burner E is placed in the position shown in the drawing, which takes hardly one second. When the requisite volume of gas (say, 1 litre of coal-gas, 1½ to 2 litres of water-gas, and 3 litres of producer-gas or semi-water gas) has been burned, the rubber tube connected with E is closed by pressing, and the temperature of the water in the calorimeter read, after agitating with the stirrer for two minutes.

The increase of temperature, multiplied by the heat equivalent of the calorimeter, gives the calorific value of the total gas burnt, which can be calculated to the *gross* value per cubic metre at normal pressure and 15°, as described above. This is quite sufficient for checking the work, and such a determination can be made in a few minutes. To obtain the *net* value, in the first instance the volume read off in the meter must be reduced to normal pressure and 0° by the well-known formula:

$$V = \frac{v \times (B - f)}{760 \times (1 + 0{\cdot}00366t)},$$

the gas in the meter being completely saturated with water; e.g., 1000 c.c. gas measured at 20° and 747 mm.

$$= \frac{1000 \times (747 - 17)}{760 \times (1 + 0{\cdot}0732)} = 896 \text{ c.c.}$$

When neglecting this reduction errors of 10 per cent. are easily made.

Most of the water formed in the combustion collects in C and is weighed in this vessel, by first emptying the water out of A, and then detaching and weighing C, after carefully drying it outside, the weight of the empty vessel having been previously ascertained. For each 10 mg. water, 6 cal. are deducted, if, as usual, the calorific value is determined for steam of 20°. C is then washed with distilled water (to remove SO_2 and H_2SO_4) and dried, to be ready for the next test.

(d) *Various Gas-Calorimeters.*—Graefe (*Z. für chem. Apparatenkunde*, 1906, pp. 320 and 723; *cf.* also Pleyer, *J. Gasbeleucht.*, 1907, p. 831) employs a nickel-coated brass cylinder, containing wire nets against which the combustion gases strike and to which hey yield up their heat. Each instrument must be gauged with a Junckers' calorimeter, as part of the gases escapes with higher temperature. The gas comes from a measuring bottle with constant overflow, and is burnt by a tuyere into a flame of or 3 cm. height.

Hempel (*Z. angew. Chem.*, 1901, p. 713) describes a calorimeter for small quantities (2 or 3 litres) of gas, and another calorimeter in *Gasanal. Methoden*, 4th ed., pp. 383 *et seq.*

Raupp's gas-calorimeter (as reported by Lux in *J. Gasbeleucht.*, 1906, p. 475) contains a copper cylinder, the lower art of which is solid, the upper part containing a thermometer ivided in tenths of a degree. Below the cylinder at an exactly measured moment a gas-flame of previously ascertained height placed, and by means of a watch the time is noted which is required to raise the temperature of the thermometer by 10°.

Stoecker and Rothenbach (*J. Gasbeleucht.*, 1908, p. 121) escribe a simple gas-calorimeter for small quantities of gas, ut Mayer and Schmiedt (*ibid.*, p. 1164) find fault with the xactness of the results obtained thereby.

The Simmance-Abady calorimeter (B. P. 27920 of 1912, made by A. Wright & Co., Westminster) resembles the Junckers instrument, but the gases travel downwards through a series of annular chambers, separated by similar chambers up which the water flows. Both thermometers of this instrument are at the same level, and by their side is a manometer tube to slow the pressure of the inlet water which must be kept constant; a damper is provided at the waste-gas exit, for the regulation of the volume of the air passing through the apparatus, and the condensed water flows through a small exit drain into a measuring cylinder.

Coste and James describe a new calorimeter which can be worked with very small volumes of gas (*J. Soc. Chem. Ind.*, 1911, p. 258).

Parr (*Progressive Age*, 1911, p. 1059; *Z. angew. Chem.*, 1912, p. 1420) burns both hydrogen and the gas to be tested at the same time and in altogether similar apparatus, and computes the calorimetric value of the second gas by comparing it with that of the hydrogen.

Strache's gas-calorimeter consists of an explosion pipette, surrounded by an air-jacket, the expansion of which is read off by a pressure gauge and directly indicates the heating value of the gas. Certain drawbacks of the original apparatus are avoided in a modification constructed by Breysig (*J. Gasbeleucht.*, 1912, lv. p. 833).

A new apparatus for estimating the heating value of gases, called *Sarco-calorimeter*, is described in *J. Gasbeleucht.*, 1913, p. 381. It consists of a U-tube filled with oil, one of the limbs being at the temperature of the surrounding air, the other limb being heated by the combustion of the gas.

Other gas-calorimeters have been described by Smith (*J. Gas Lighting*, cxx. p. 1051); Macklow, Smith, and Pullen (B. P. 1905, of 1911).

Weyman (*J. Soc. Chem. Ind.*, 1914, p. 11) discusses the difference between the calculated and determined calorific values of coal-gas.

X. DETERMINATION OF THE ILLUMINATING POWER OF GASES.

This operation, which, of course, is only carried out with coal-gas or other gases used for illuminating purposes, does not belong to the domain of technical gas-analysis. We shall therefore only state that it is carried out by means of *photometers*, by comparing the flame to be tested with a standard light, usually the pentane lamp, the Hefner amylacetate lamp, or the carbon-filament incandescent lamp.

Very many photometers have been devised, of which that designed by Bunsen is most widely used. For a detailed treatment of this subject we refer to the chapter on gas-manufacture by Pfeiffer, in Lunge and Berl's *Chemisch-technische Untersuchungsmethoden*, vol. iii. pp. 320 *et seq.* (1911); English translation by Keane, vol. ii. pp. 697 *et seq.*

SPECIAL METHODS FOR DETECTING AND ESTIMATING VARIOUS GASES OCCURRING IN TECHNICAL OPERATIONS.

OXYGEN.

The estimation of oxygen has been described in a number of places in the preceding chapters, especially pp. 119 *et seq.*

We shall now describe some special apparatus and methods for this purpose.

Lindemann's apparatus is shown in Fig. 93. The measuring-tube A has a three-way cock at the top, but no tap at the bottom. It contains altogether 100 c.c., 75 c.c. of this in the globular and 25 c.c. in the cylindrical part, which is divided into tenths of a cubic centimetre. The levelling bottle C contains water, the absorbing vessel B thin sticks of phosphorus and water up to the mark. The gas is introduced through the pinchcock arrangement connected with the three-way cock; otherwise the manipulation is exactly as with the Orsat apparatus (p. 66).

This apparatus serves for the rapid estimation of oxygen in air, both ordinary and that from graves, respiration, Weldon's oxydisers, Bessemer converters, vitriol chambers, etc., especially also in the waste gases from sulphuric acid chambers, from the Deacon process, etc.

Method of Pfeiffer (*J. Gasbeleucht.*, 1897, p. 354). This is specially intended for estimating the small quantities of oxygen occurring in coal-gas. This slight proportion of oxygen has no sensible influence on its quality, but it should be ascertained with reference to the manufacture of the gas, since it has become quite general to mix 1 or 2 vols. per cent. oxygen with crude gas before purification, in order to bring about a partial regeneration of the purifying mass already in the boxes. The regenerating air is introduced into the crude gas by a branch pipe of the gas tubing in front of the aspirator; the air thus introduced is measured from time to time by means of an interposed meter, and the velocity of the air-current regulated accordingly. Of course it is unavoidable that somewhat great varieties occur in the admixture of air with the gas, as this depends on the action of the aspirator and the partial vacuum produced by this.

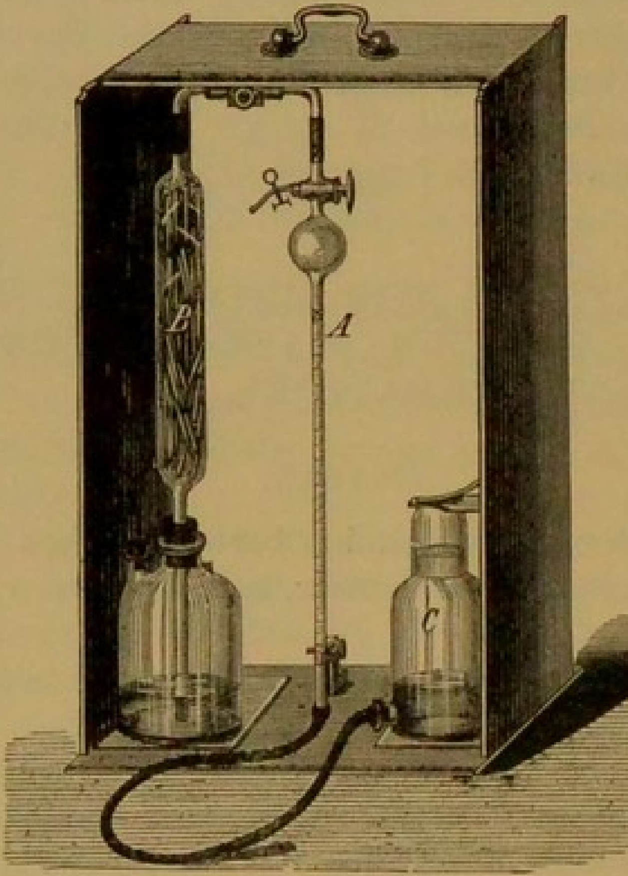


FIG. 93.

Such small percentages of oxygen, according to Pfeiffer, can be estimated colorimetrically by the formation of strongly colouring matters, taking place when a caustic solution is brought into contact with pyrogallol in the presence of oxygen, which can be easily done in a Bunte burette. One hundred c.c. of gas is introduced into the burette and measured in the way above described (p. 61). The water is now drawn off from the bottom of the burette and replaced by 5 c.c. caustic potash solution (1 : 2). The height occupied by this quantity of liquid is marked once for all on the burette by a slight file-stroke. The funnel above ought at first to contain water only in the capillary. Into this funnel 0·2 g. pyrogallol is put and covered with 2 c.c. water, which dissolves it. The solution is drawn into the burette, leaving a drop behind which closes the capillary. The oxygen in the burette is absorbed by shaking for two minutes. Now from below a sufficient quantity of water, free from oxygen (see below), is allowed to enter, until a certain mark, say 0, has been reached. Two minutes after finishing the agitation, the colour produced is compared with that shown in a wide test-tube, containing 10 c.c. of water, into which decinormal iodine solution is run drop by drop from a burette, until the colours are identical. The observation is best made by holding both tubes with one hand against the light, putting the other hand across them and leaving only a gap between the fingers for looking through. The number of drops required corresponds to a certain percentage of air, empirically produced as below, which can be read off directly from a small table.

The decinormal iodine solution employed for comparison contains 2 parts potassium iodide to 1 part free iodine; in dilute solutions the colour is exactly like that of the galloflavine, produced from the pyrogallol. In order to establish the "titre" of this iodine solution, artificial mixtures, containing ½, 1, 2, 3 per cent. of air are treated in the Bunte burette with alkaline pyrogallol in the above-described way. When the burette has been filled with water up to the zero mark, 10 c.c. of water is put into the test-tube intended for receiving the comparing liquid, and from a small tube so much iodine solution is added, drop by drop, that the liquid shows exactly the same colour as that in the burette. The eye permits easily to distinguish the difference of colour produced by a single drop. The observation is always made two minutes after finishing the agitation. For instance the following number of drops was required for various contents of air: 0·5 per cent. air = 4 drops; 1 per cent. air = 11 drops; 2 per cent. air = 33 drops; 3 per cent. air =66 drops. These are average values from a number of tests, the outside limits of which at the worst would cause an error of ¼ per cent. air (=0·05 per cent. oxygen). It is recommended to enter the values found on "millimetre paper" in a curve, the air percentages as abscisses, and the number of drops as ordinates, in order to save the trouble of making interpolations. The values found for air are converted into percentages of oxygen by multiplying them with 0·21.

The mixtures of gas and air required for this comparison are best produced in the burette itself. About 100 c.c. of gas is in the first place treated for the removal of oxygen by any of the well-known methods. Then the quantities of air: 0·5, 1, 2, or 3 c.c., are measured off by means of a pipette, divided from the point upwards, by connecting its bottom end with the rubber tube of the small water reservoir belonging to the Bunte burette. The water is allowed to rise up to the desired mark in the pipette, the point is put into the short rubber tube usually placed over the lateral opening of the three-way cock, this cock is turned 180°, and the air is driven from the tube into the burette by means of water run in at the top. Then the cock is turned back again.

The air contained in the water used for filling the burette up to the zero mark may amount up to 0·1 c.c. oxygen. This is but a small quantity, and it is probably always much the same; it can be neglected, since always the same quantity of water is employed. If you wish to be entirely independent of this constant, especially in order to get a sharper result for qualitative tests, you must prepare for these tests *water free from oxygen.* Pfeiffer obtains this by contact with zinc, made specially active by covering it with water containing 1 or 2 drops of cupric sulphate solution, pouring off the liquid after a quarter of an hour, and washing with water. Granulated zinc treated in this manner is put into a ½-litre Woulff's bottle. Through one of the necks of this bottle, *a*, a tube goes down to the bottom, closed there by a plug of cotton-wool, in order to retain any flakes of zinc oxide; the upper end carries a rubber tube about 10 cm. long, with pinchcock. The second neck is closed by a doubly perforated stopper, through which pass two short tubes, *b* and *c*. Tube *b* projects a little into the bottle; tube *c* ends below flush with the stopper, and at the top is closed by a short rubber tube, closed by a glass rod. The bottle is filled with water, and this is saturated with coal-gas (tube *a* being connected with the gas pipe, tube *b* with an aspirator). By jerking the bottle against the palm of the hand, any air or gas bubbles between the bits of zinc are removed. Now connect tube *b* with the rubber tube of the air reservoir belonging to the Bunte burette, and thus place the bottle under pressure. By lifting the stopper *c* allow the gases, collected at the top, to escape. After a few hours the water in the bottle will be free from oxygen, which is tested for by making a sample of it alkaline and adding a drop of manganous chloride solution, which should produce a perfectly white precipitate of hydrated manganese protoxide. For use the water is taken out of tube *a* by allowing it, after opening the pinchcock, to rise into the rubber continuation and from this into the burette, the point of which has been connected with that rubber pipe. The water running down from the upper reservoir at once comes into contact with the zinc; since it is prevented by this from moving freely, it does not, when gradually used, get to the bottom of the bottle until it has yielded up all its oxygen to the zinc.

Before estimating the oxygen in crude coal-gas, first the sulphuretted hydrogen must be removed by caustic alkali, as this gas in the presence of oxygen imparts to the pyrogallol solution a Burgundy-red colour.

Another very simple method has been worked out by Pfeiffer (*J. Gasbeleucht.*, 1898, p. 605) for the determination of the "*neutral zone*" *of combustion* in the flues of retort-furnaces (or other fireplaces), *i.e.*, the point at which free oxygen first appears in the mixed gases, for which purpose a quantitative estimation of the oxygen is unnecessary. The apparatus, shown in Fig. 94, consists of a calcium-chloride tube, about 30 c.c. long, in which are placed a few thin sticks of yellow phosphorus, about 15 c.c. long. The lower end is closed with a cork fitted with a doubly-bent glass tube, and the whole is placed in a jar containing sufficient water to cover the phosphorus and to prevent its oxidation by the air. To use the apparatus, the tube containing the phosphorus is lifted out of the jar and the water allowed to drain out; the bent glass tube is then connected to the porcelain tube through which the sample is drawn from the flues, the upper end to an aspirator, and the tube is then replaced in the water to protect it from the heat radiated from the brickwork. The temperature of the water must not be below 15°, as phosphorus does not combine with oxygen below that temperature. The flues are then tested in order from top to bottom; as soon as oxygen is present in appreciable quantity, thick white fumes of phosphorus oxides are formed. A slight mist is formed at each suction of the stroke of the aspirator, due to the deposition of moisture owing to the cooling of the gas by expansion; but this is quite distinct in appearance from the phosphorous fumes, and cannot be mistaken for them.

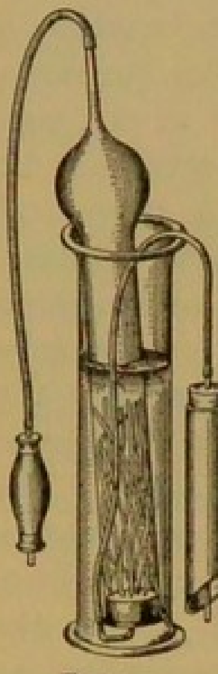


FIG. 94.

Lubberger (*J. Gasbeleucht.*, 1898, p. 695) employs the following method for the estimation of oxygen: bringing the gas in a Bunte burette into contact with alkali and manganous hydrate, whereby manganic hydrate is formed. After acidulating with hydrochloric acid and adding potassium iodide, the liberated quantity of iodine, which is equivalent to the oxygen originally present in the gas, can be titrated with sodium thiosulphate.

The following liquids are required for this process: (*a*) a solution of potassium iodide (10 g. NaOH, 35 g. potassium sodium tartrate, 8·5 g. KJ, dissolved in 300 c.c. water); (*b*) manganese solution (10 g. $MnCl_2$, dissolved in 100 c.c. water); (*c*) centinormal thiosulphate solution (2·48 g. $Na_2S_2O_3 + 5H_2O$, dissolved in 1 litre); (*d*) water free from oxygen, prepared by the process described *suprà*, in connection with Pfeiffer's method. The gas, about 100 c.c., is measured in the burette. The water is drawn off from below, and 3 c.c. of the potassium-iodide solution is allowed to enter into the burette from here, as well as 1 c.c. of the manganese solution through the top funnel. The whole is vigorously shaken up for ten minutes, so that the liquid is jerked all over the inside of the burette. Now 1 c.c. concentrated hydrochloric acid is allowed to enter from below, and the burette agitated. Any oxygen present in the gas is already now indicated by iodine being set free and causing a yellow coloration. In the acid liquid no more iodine is liberated by oxygen. The contents of the burette are washed into a beaker by pouring water into the top funnel, starch solution is added, and the titration made by adding centinormal thiosulphate solution until the blue colour has been destroyed. From the quantity of thiosulphate used 0·3 c.c. must be deducted, as shown by experience. Each cubic centimetre of thiosulphate indicates 0·12 vol. per cent. of oxygen, if 100 c.c. gas has been operated upon. Here also the H_2S must be previously removed. (Pfeiffer did not find this method to give satisfactory results.)

The apparatus and method of Chlopin (*Arch. f. Hygiene*, 1900, p. 323) is more particularly intended for hygienic purposes; it is described in Lunge-Keane's *Technical Methods*, vol. i., pp. 867 *et seq.* James Miller (*J. Soc. Chem. Ind.*, 1914, p. 185) absorbs the oxygen dissolved in water by ferrous sulphate.

Hale and Mella (*J. Ind. and Engin. Chem.*, 1913, p. 976) studied the influence of the presence of nitrite for the determination of oxygen dissolved in water by L. W. Winkler's method (p. 218). They found this method to be very easy, rapid, and accurate. Nitrite as present in the usual run of waters has no appreciable effect upon the accuracy of the results; but if present in quantities upward of 0·2 per metre it increases the results by a catalytic reaction. This effect may be counteracted by the use of potassium acetate solution, or sodium acetate crystals, to neutralise the hydrochloric acid before exposure to the air.

Reaction of Nitric Oxide with Oxygen.—This reaction varies according to the excess of one or the other of these gases, and whether moisture is present or not. Already Priestley and Cavendish tried to estimate the oxygen in atmospheric air in this manner, but Berthelot (*Comptes rend.*, lxxvii. p. 1448) and Lunge (*Ber.*, 1885, p. 1376) did not get satisfactory results thereby. The better results of Wanklyn and Cooper (*Chem. News*, lxii., pp. 155 and 179) have been proved to be unreliable by de Coninck (*Z. angew. Chem.*, 1891, p. 78). According to Klinger (*Ber.*, 1913, p. 1745) oxygen can be correctly examined by employing an excess of nitric oxide, by strictly keeping out moisture from the gases, and especially by employing perfectly dry sticks of caustic potash for absorbing the nitrogen trioxide formed by the reaction: $4NO + O_2 = 2N_2O_3$, in which case one-fifth of the contraction observed after the treatment with KOH is due to the oxygen.

Calafat y Leon (B. P. 4141 of 1913; Ger. P. 267493; *Z. angew. Chem.*, 1914, ii. p. 9) makes use of the fact that the temperature of a flame is dependent on the proportion of oxygen in the air supporting combustion. A thermometer of special form is employed, the bulb being surrounded by spongy platinum wires, which act as the burner. The air is passed over wool and pumice saturated with methyl alcohol, and combustion commences when it comes in contact with the spongy platinum.

Léon (Fr. P. 454109) also estimates the oxygen in air by saturating this with methyl alcohol, and passing the mixture through a platinum sponge lamp which influences a pyrometer, the indication of which is dependent on the degree of energy of the combustion.

Binder and Weinland (*Berl. Ber.*, 1913, p. 255) discover and estimate free oxygen by the deep red colour produced in an alkaline solution of pyrocatechine and ferrous sulphate, through the formation of tri-pyrocatechine-ferri-acid: $[Fe(C_6H_4O_2)_3]H_3$. They carry this out in a glass cylinder, through the cork of which passes the gas-pipe and a drop-funnel; a little below the cork a side-tube branches off, connected with a glass valve. The dry cylinder is charged with 0·4 g. pure Mohr's salt, free from ferric peroxide, and 0·5 g. pyrocatechine. The funnel is filled with boiled water, and pure hydrogen, freed from any oxygen by passing it through alkaline sodium hydrosulphite solution, is passed through. In any case a slight red colour is produced, but a strong colour ensues if the gas to be tested contains any oxygen. The formation of the above-mentioned compound may also be used for a quantitative estimation of the oxygen present in the gas by means of a Hempel pipette which must be vigorously shaken for five minutes.

L. W. Winkler (*Z. angew. Chem.*, 1911, pp. 341 and 831; 1913, p. 134) estimates oxygen dissolved in water, approximately by a mixture of "adurol" with the ammoniacal solution of ammonium bromide, or with borax, which produce a deep red colour.

Haldane's apparatus is based on the observation that a candle flame is extinguished with a certain dilution of the oxygen ; it is contended by Schorrig (*Abstr. Amer. Chem. Soc.*, 1913, vii. p. 1993) that this gives a better idea as to the suitability of mine air for respiration than its chemical analysis, as the aqueous vapour contained in the air is thereby taken into account.

J. J. van Eck (*Z. anal. Chem.*, 1913, p. 753) employs for this estimation Romijn's water-pipette.

OZONE.

The usual *qualitative* test for ozone is the blue colour produced in a solution of (or on a test-paper impregnated with) potassium iodide and starch, through the liberation of iodine. A special test-paper for this purpose is found in the trade as "Houzean's test-paper," improved by Arnold and Mentzel (*Ber.*, 1902, p. 1324). Of course this test can only be made in the absence of free chlorine, bromine, hydrogen, peroxide or nitrous vapours, if (as formerly usual) an acidified solution of KI is employed; but in the absence of chlorine the *immediate* blue coloration of a *neutral* solution of KI and starch is a good test for ozone, since the colour comes out only very slowly in presence of hydrogen peroxide and not at all with nitrites.

Engler and Wild (*Ber.*, 1896, p. 1940) test for the presence of ozone by passing large quantities of the air under examination first through finely-divided chromic acid, in order to remove any hydrogen peroxide, and then into a glass tube, in which are placed, side by side, a manganese-sulphate paper, which is coloured brown by ozone (through the formation of Mn_3O_4) but not by chlorine, and a thallous-oxide paper, which remains colourless in presence of nitrous acid, but is turned brown by ozone. If both papers are coloured, ozone is present.

The qualitative detection of ozone can be performed most easily and distinctively by tetramethyl-di-*p*-diaminodiphenylmethane, usually designated as "tetramethyl base," either in alcoholic solution or as a test-paper. Ozone produces with it a violet, nitrogen oxides a straw-yellow coloration; hydrogen peroxide gives no reaction (Arnold and Mentzel, *Ber.*, 1902, pp. 1327 and 2902; F. Fischer and H. Marx, *ibid.*, 1906, p. 2555).

A very complete paper on the detection of ozone in the presence of nitrogen tetroxide and hydrogen peroxide is that of Keiser and M'Master (*Amer. Chem. J.*, 1908, p. 967).

The *quantitative* estimation of ozone in air, etc., is usually carried out by passing the gas through a solution of potassium iodide and titrating the iodine set free. Formerly an acidified solution was employed, but this caused errors up to an amount of 50 per cent., which are, however, avoided according to Lechner (*Z. Elektrochem.*, 1911, xvii. p. 412) by employing an alkaline solution of KI. Czakó (*J. Gasbeleucht.*, 1912. lv. p. 768) carries this method out in a Bunte burette. The burette, filled with distilled water, is connected in an inverted position by means of a mercury seal with the gas-holder, and about 100 c.c. of the gas is introduced. After reading the volume, the water is drawn off, about 10 or 12 c.c. of the alkaline KI-solution is introduced, the burette is shaken for three minutes, its contents are run into a flask and the burette is rinsed. The absorbing liquid is acidulated with 5 c.c. of fifth-normal sulphuric acid, and the separated iodine is titrated with sodium thiosulphate. This method is applicable wherever the gas contains upwards of 0·01 vol. per cent., *i.e.,* 0·02 mg. in 100 c.c. For smaller concentrations he employs a bottle filled with glass beads, interposed between the source of ozone and the gas-meter. The reaction is:

$$O_3 + 2KI + H_2O = O_2 + 2KOH + 2I.$$

One c.c. *N*/1000 sodium thiosulphate solution (0·2483 g. per litre) indicates 0·024 mg. O_3.

Treadwell and Anneler (*Z. anorg. Chem.*, 1905, lxviii. p. 86) also recommend this method, so do Rothmund and Burgstaller (*Chem. Zentralb.*, 1913, i. p. 2178), who estimate ozone and hydrogen peroxide alongside of each other by allowing a weak acid to act upon potassium bromide, adding potassium iodide in slight excess, and titrating the iodine, set free by the ozone, by means of sodium thiosulphate.

Brach (*Chem. Zeit.*, 1912, p. 1325) employs for the estimation of ozone apparatus, composed with ground-glass connections, silk tubes impregnated with wax, and flexible steel pipes.

Krueger and Moeller (*Phys. Zsch.* 1912, xiii. p. 729; *Chem. Zentralb.*, 1912, ii. p. 748) employ for the analytical estimation of ozone its strong absorption within the wave lengths 200 to 300 mm. They assert this optical method to be essentially more delicate than any chemical methods.

HYDROGEN PEROXIDE.

The investigations of Schöne (*Z. anal. Chem.*, 1894, xxxiii. p. 137) are the most important in this direction. As reactions for this compound he describes, first, the blue coloration of perchromic acid, caused by adding a trace of potassium bichromate to the solution, covering this with a layer of ether, and shaking up with a trace of sulphuric acid; secondly, the blue coloration with potassium iodide and starch on addition of a trace of ferrous sulphate (Schönbein); thirdly, the blue colour produced by guajacol-malt extract. Details in Lunge-Keane's *Technical Methods*, i. pp. 879 *et seq.*

Determination of Ozone and Hydrogen Peroxide in the Presence of each other.—Rothmund and Burgstaller (Wiener, *Monatshefte*, 1913, xxxiv. p. 693; *Amer. Abstr.*, 1913, p. 2528) employ molybdic acid as a catalyser in the reaction between the hydrogen peroxide and potassium iodide. At a temperature of about 0° the weakly acid solution (about 0·01 normal) is added to a potassium bromide solution, potassium iodide in excess of the amount equivalent to the ozone present is added, and the free iodine titrated with a centinormal solution of sodium thiosulphate. The amount of ozone is calculated from this. Next are added 10 cm. of seminormal potassium iodide solution, 1 cm. of decinormal sodium molybdate solution, and 15 cm. of dilute sulphuric acid (1 : 5 water). After five minutes the liberated iodine is titrated, and the equivalent amount of H_2O_2 calculated.

Pring (*Chem. News*, 1914, vol. 109, p. 73), as the result of work done on the estimation and distinction of ozone, nitrogen peroxide, and hydrogen peroxide at high dilutions, states that the reaction of potassium iodide on those substances shows the following characteristics:—With ozone the ratio of the different products formed is a function of the concentration of the gas and of the total amount passed. With a very dilute gas no iodate is formed by only hypoiodite and free iodine, and no potassium hydrate. But at temperatures below $-27°$ this relation does not hold.

With nitrogen peroxide mainly iodate is formed, whatever the dilution of the gas. In presence of an acid solution of potassium iodide, nitrogen peroxide, even when present in minute quantities, continually liberates iodine from the reagent in the presence of air, which is a very delicate test for this gas.

Hydrogen peroxide, at high dilution, reacts with potassium iodide like ozone, but a distinction can be made between these gases by means of a solution of tetanium sulphate in sulphuric acid, which becomes yellow in presence of very little hydrogen peroxide, but is unaffected by ozone.

CARBON DIOXIDE.

This compound can be estimated by most apparatus for technical gas-analysis described in previous chapters, and in this place we mention only some apparatus and methods specially intended for it.

The apparatus of *Cl. Winkler* (*Techn. Gas-Analysis*, p. 91), shown in Fig. 95, is specially intended for the estimation of small quantities of CO_2 in the air of coal-pits, wells, caves, subsoil, tombs, in chimney-gases poor in CO_2, and analogous cases. It is almost identical with Lindemann's apparatus for the estimation of oxygen (p. 212, Fig. 93), but in the place of the phosphorus-vessel, used in the latter, it contains a cylinder B,

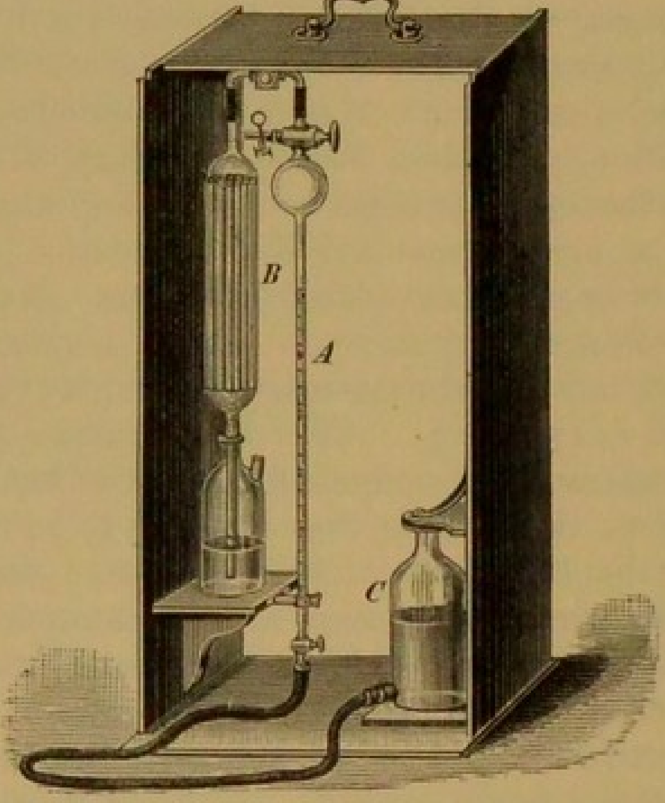


FIG. 95.

filled with glass tubes for increasing the absorbing surface, the bottle below being charged with a solution of caustic potash. The manipulation is just like that of Lindemann's apparatus.

The apparatus of *A. Lange*, intended for estimating CO_2 in liquid carbon dioxide and in the natural sources of this gas, has been described *suprà*, p. 55.

Pettenkofer's classical method, which is specially intended for hygienic purposes, is described in Lunge-Keane's *Technical Methods*, i. pp. 870 *et seq.*; also *Haldane's* apparatus, pp. 873 *et seq.*, and that of *Lunge and Zeckendorf* for the approximate determination of CO_2 in air, p. 875.

Ludwig W. Winkler (*Z. anal. Chem.*, 1913, p. 421) recommends Pettenkofer's method as most convenient for the estimation of CO_2 in air, and describes a special apparatus for that purpose.

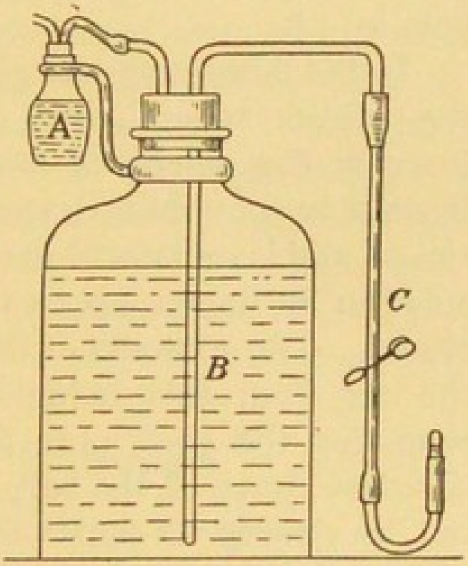


FIG. 96.

We shall in this place describe the modification of the Pettenkofer method, introduced by *Hesse* (Eulenberg's *Vierteljahrsschrift f. gerichtl. Medizin*, N. F., xxx. p. 2; translated in Dennis' *Gas-Analysis*, p. 378), as it has proved itself to be very satisfactory. The CO_2 in a known volume of air is absorbed by a solution of barium hydroxide of known strength, and the excess of $Ba(OH)_2$ is determined by titration with oxalic acid, with phenolphthalein as indicator. For this method the following solutions are used: (1) A solution of 1 kg. barium hydroxide and 50 g. barium chloride in 5 litres of distilled water; (2) a dilute solution of barium hydroxide, prepared by adding 30 c.c. of the solution No. 1 to a litre of water, or else by directly dissolving 1·7 g. of a mixture of 20 barium peroxide + 1 barium chloride in 1 litre of water, and adding phenolphthalein up to a faint pink colour. This solution is kept in a bottle, Fig. 96, through the cork of which passes (1), a tube leading to a small bottle A, containing a caustic potash solution, for the purpose of freeing the entering air from carbon dioxide; (2), a syphon-tube B, continued into an india-rubber tube with stopcock C; (3) a solution of 5·6325 g. of crystallised oxalic acid in 1 litre of water, 1 c.c. of which is equivalent to 1 c.c. of CO_2; (4) a solution of 1 part phenolphthalein in 250 parts alcohol.

The samples of air are collected in thick-walled Erlenmeyer flasks of 100 to 500 c.c. capacity, supplied with tightly-fitting, double-bore rubber stoppers. The openings in the stoppers are closed by pieces of glass rod, rounded at the lower end and widened at the upper end. The apparatus further comprises a 10 c.c. pipette, and a burette of 10 to 15 c.c. capacity, graduated in $\frac{1}{10}$ c.c., with glass stopcock and a tip 8 cm. long.

The samples of air are collected by completely filling the flasks with distilled water of the same temperature as the surrounding air, pouring out the water and immediately inserting the rubber stoppers, care being taken that the flask is not warmed by the hand, and that no air exhaled by the operator gets into it.

In the laboratory the glass plug is removed from the end of the rubber tube C, Fig. 96, the tip of the 10 c.c. pipette is inserted, the pinchcock is opened, and some of the solution of barium hydroxide is drawn up in the pipette, which is thereby rinsed, and is reinserted in the tube, whereupon barium hydroxide solution is drawn up to the zero mark and the pinchcock is closed. The contents of the pipette are then run into the flask, the air from this being allowed to escape by momentarily removing the glass plug from the other hole of the stopper. The last drops of the baryta solution in the pipette are driven out by closing its upper end with the finger, and warming its wider portion with the hand. The pipette is then removed, and the stopper closed with the glass plug. The closed flask is allowed to stand from fifteen to twenty minutes with occasional shaking. The barium hydroxide should be present in such excess that not more than one-fifth of it reacts with CO_2. If, therefore, a large sample of air is employed, or if the CO_2 contained in it is unusually high, 20 or 25 c.c. of the solution of barium hydroxide should be used.

The strength of the baryta solution is determined by filling the burette to the mark with the standardised solution of oxalic acid (*suprà*, No. 3), inserting the tip of the burette through one opening of a two-hole rubber stopper, placing this in the neck of a 100 c.c. flask, and then running into this oxalic acid solution almost sufficient to neutralise 10 c.c. of the baryta solution. Ten c.c. of the latter is then introduced into the flask in the manner above described, and more oxalic acid is then carefully added until the pink colour of the indicator just disappears. This colour will frequently reappear on standing, but no notice should be taken of this.

The excess of barium hydroxide in the sample flask is then titrated by filling the burette to the mark with the oxalic acid solution, inserting its tip through one of the openings of the stopper and running in the oxalic acid, first rapidly, afterwards drop by drop. The increase of pressure in the flask is from time to time relieved by momentarily lifting the glass plug in the other hole of the stopper. As before, the end-point of the reaction is the *first* disappearance of the pink colour.

The temperature and barometric pressure of the outer atmosphere are then read; 10 c.c. is deducted from the volume of the sample flask to allow for that of the baryta solution introduced, and the remaining volume corrected to standard temperature and pressure. The number of cubic centimetres of the oxalic acid solution required to neutralise the excess of the baryta solution is deducted from the volume of oxalic acid required to neutralise 10 c.c. of the baryta solution. If we call this difference $= n$, the amount of carbon dioxide in the sample is calculated by the following formula:

$$n/10 \text{ volume of air sample} = x : 10{,}000,$$

in which x represents the parts of CO_2 per 10,000 of air.

In lieu of phenolphthalein, Moir (*Abstr. Amer. Chem. Soc.*, 1913, p. 3092) recommends, as yielding rather more accurate results in titration, benzaurine or thymolphthalein.

Pfeiffer describes his way of making very accurate estimations of carbon dioxide in *illuminating gas*. The estimation by potassium hydroxide is not very accurate, because this agent also tends to absorb some of the hydrocarbon vapours present. When greater accuracy is required, the CO_2 is estimated gravimetrically or volumetrically; the former by absorbing it in a soda-lime tube, the latter by Pettenkofer's method, absorption in titrated baryta water. For the former method the gas, if unpurified, must be first freed from ammonia by passing it through dilute acid, and from tar-fog and sulphuretted hydrogen by passing it through hydrated ferric oxide. It is then passed through a meter, dried by calcium chloride, and passed into a weighed soda-lime tube, the last part of which is filled with calcium chloride to retard the moisture. Each gramme of CO_2 retained here is = 544 c.c. of CO_2, measured in the moist state at 15° and 760 mm.

For the volumetric estimation by means of baryta water, Pfeiffer employs a bottle of about 2 litres capacity, with a cork through which passes a small dropping-funnel of about 50 c.c. capacity reaching almost down to the bottom, and a right-angled exit-tube, as shown in Fig. 97. The exact capacity of the bottle is determined by weighing it first empty, and then filled with water, after removing the exit-tube, and filling the stem of the funnel with water up to the stopcock; the different weights in grammes = the contents in cubic centimetres. To fill the bottle with gas in the moist state three drops of water are put in, the bottle is inverted, and gas passed in through the dropping-funnel and out through the exit-tube; a moderate stream of gas during two or three minutes will drive out all the air. The exit-tube is then removed and replaced by a glass plug, the tap of the funnel is closed, and the gas tube disconnected. The stopcock is then again opened for a second to make the gas in the bottle assume atmospheric pressure, and the state of the barometer and thermometer in the room noted.

FIG. 97.

When the gas in the funnel has been replaced by air, 50 c.c. baryta water of known strength (say, 20 g. barium hydroxide per litre) and a little phenolphthalein solution is run into the funnel, and thence, by carefully opening the cock, into the bottle, washing the funnel with water, but taking care that its delivery pipe always remains filled with water. The liquid is easily run in, since on the one hand the carbon dioxide is quickly absorbed, and on the other hand the gas is compressed by the column of water standing in the tube of the dropping-funnel. The bottle is shaken now and then, and the absorption may be taken as complete in thirty minutes. Now the cock of the funnel-pipe is opened, the rubber stopper is taken out, and any adhering baryta solution washed into the bottle, the liquid adhering to its walls washed down, and now the liquid at once titrated in the bottle itself with decinormal oxalic acid and phenolphthalein.

While the absorption in the bottle is going on, the titre of the baryta solution is established in the same way. The difference of both titrations, n, shows the baryta consumed, expressed as decinormal solution. One c.c. decinormal baryta corresponds to 0·0022 g. CO_2, or 1·119 c.c. CO_2 at 0° C. and 760 mm. If the contents of the bottle in cubic centimetres is called v, the temperature $= t$, the vapour pressure of water at that temperature $= c$, the height of the barometer $= b$, the volume-percentage carbon dioxide, reduced to standard volume, is:

$$CO_2 = \frac{n \times 1.119 \times 100}{v \times \frac{(b-e)273}{760(273+t)}} = \overbrace{\frac{1.119 \times 100 \times 760}{273v}}^{\text{Constant.}} \times \overbrace{\frac{n(273+t)}{b-c}}^{\text{Variant.}}$$

If v has been measured once for all, in lieu of that part of the formula which is marked "constant," a simple figure is put in.

Apparatus of Rüdorff (*J. Gasbeleucht.*, 1865, p. 358; *Berl. Ber.* xiii. p. 130).—This apparatus, which is very easily handled even by persons not accustomed to gas-analysis, is frequently employed for estimating the CO_2 in coal-gas, especially in its unpurified state. The large volume employed (1 litre) admits of greater accuracy than the ordinary methods of volumetric gas-analysis, where usually only 100 c.c. of gas are examined. The apparatus is shown in Fig. 98.

Its principle is: confining the gas to be examined in a bottle G of known capacity under atmospheric pressure, and absorbing the carbon dioxide by caustic potash solution which is run in from the burette P, divided into $\frac{1}{5}$ c.c., placed on the bottle, at such a rate that the gaseous space vanishing is replaced by liquid, *i.e.*, that the pressure in the bottle is not changed. The quantity of liquid run out of the burette indicates the volume of the CO_2 absorbed.

The apparatus is made entirely of glass. The absorbing bottle G has at the top three necks closed by glass taps, of which A serves for introducing the gas, C is connected with the burette P, and B with the exit-tube. A and C are simple one-bore cocks, B is a three-way cock, one of whose bores is connected with the water-pressure gauge M, the other angular tail-bore being open to the outside air. The bottle G is suspended by means of the spring-clamp F in a large vessel K, filled with water in order to keep the temperature constant. When examining crude gas, first hydrogen sulphide and ammonia must be removed by washing the gas with a solution of lead acetate containing a little free acetic acid and contained in two washing bottles in front of the apparatus. After all joints have been made gas-tight by greasing with tallow, the gas is passed in at A, the air escaping by the tail-bore of B; C during this time is closed. After passing the gas through for ten minutes, tap B is turned 180°, so that now the communication with the outer air goes through the pressure gauge M. Now tap A is closed and the communication with the gas-conduit interrupted. If now tap B is placed in the position shown in the figure, the pressure gauge M will indicate any over-pressure still existing in the bottle. This plus-pressure is destroyed by turning tap B for a moment so as to allow the gas to escape outside, and this proceeding is repeated until the pressure gauge M, when tap B is again in communication with it, indicates atmospheric pressure by showing the same level of water in both arms of the U-tube during a longer observation. Now from the burette P, previously filled up to the mark O, potash solution

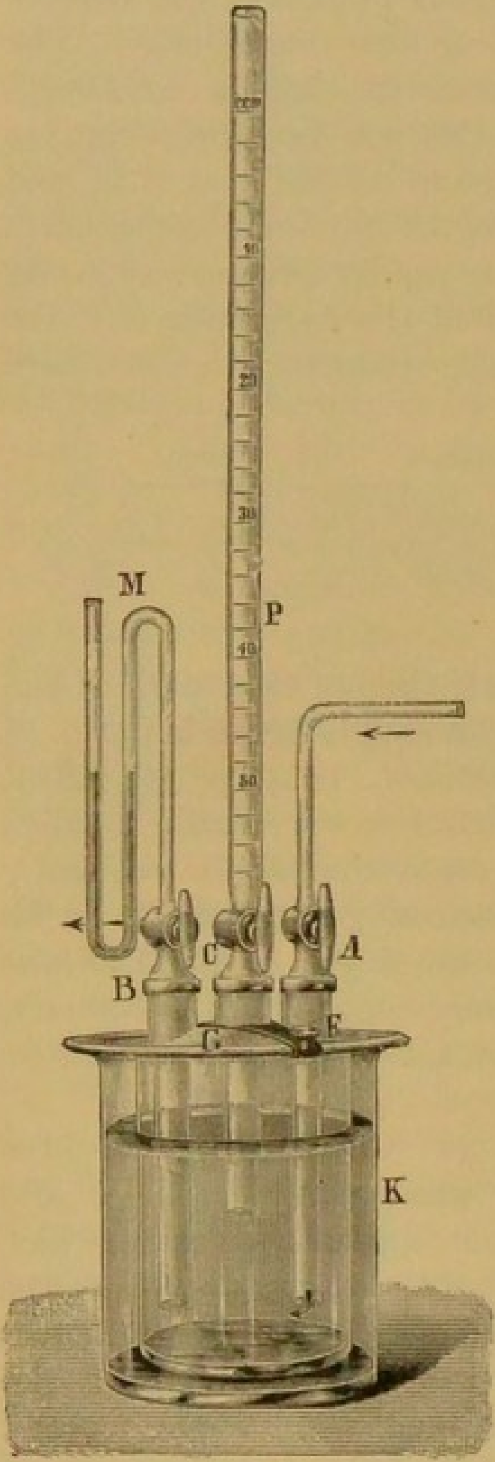


FIG. 98.

is cautiously run into bottle G, always observing the pressure gauge M. At first this will show an increase of pressure which, however, rapidly vanishes, the CO_2 in G being absorbed by the potash solution. This solution is run in at the rate as the absorption is proceeding, so that the state of the pressure gauge is not essentially altered. Towards the end a few minutes are allowed to elapse, in order to make sure that there is no more change in the volume of pressure. The absorption may be hastened by cautiously shaking the bottle, which for this purpose is got hold of by the two necks A and B, and taken out of K. When the reaction is finished, so much liquid is run from P into G that the atmospheric pressure is re-established. The burette P is read off, and the cubic centimetres run out of it indicate the same volume of CO_2, which is calculated upon the contents of bottle G.

The apparatus supplied by the dealers hold exactly 1130 c.c., and are provided with a table from which the volume-percentages of carbon dioxide corresponding to the cubic centimetre of potash solution consumed are directly read off (1 c.c. of liquor = 0·0885 per cent. CO_2); *e.g.*, 18 c.c. of potash liquor used = 1·593 per cent. CO_2 by volume. (Pfeiffer considers this apparatus as more interesting than practical.)

Göckel (*J. Gasbeleucht.*, 1912, p. 823) has modified this apparatus so as to have only one neck and one glass-tap with two bores (sold bv Dr Heinrich Göckel & Co., Berlin, Louisenstrasse 21).

Other apparatus for this purpose have been described by Pettersson and Palmquist (*Berl. Ber.*, 1887, p. 2129, and in *Z. anal. Chem.*, xxv. pp. 467 to 484). Their apparatus has been made more easily portable by R. P. Anderson (*J. Amer. Chem. Soc.*, 1913, xxxv. p. 162) by reducing its size to about half, and providing a copper coil, which dips into the water of the glass vessel, and allows of rapidly bringing the temperature of the gas sample to that of the apparatus.

Dejeanne (*Bull. Soc. Chim.*, 1913, p. 556; *Z. angew. Chem.*, 1914, ii. p. 15) absorbs the CO_2 by baryta water of known strength, converts the excess of baryta into chloride by means of magnesium chloride, and estimates the Ba in an aliquot portion of the filtrate gravimetrically.

Apparatus for the Rapid and Continuous Estimation of

Carbon Dioxide in Fire-Gases, etc.—During recent years the methods and apparatus for a rapid and continuous analysis of gaseous mixtures have come more and more into use. Many of these, described in the technical periodicals, are not obtainable in trade; and in the following we shall only mention the more important apparatus of those which are actually employed in practice, and are obtainable from special firms.

In most cases such apparatus have been constructed for a rapid or continuous estimation of the percentage of carbon dioxide in fire-gases, as a control of the firemen, but these apparatus are also applicable for the estimation of other gases.

A very rough but ready estimation of the carbon dioxide in smoke-gases can be made by ascertaining their *specific gravity.* A very expeditious way of doing this is the *Gas-balance of Lux* described *suprà*, p. 183 (sold by the Vereinigte Fabriken für Laboratoriumsbedarf, Berlin N.). An improvement on this is the *Schnellgaswage of G. A. Schultze*, Berlin-Charlottenburg, in which the indications of a micromanometer give directly the percentage of carbon dioxide. The same firm also sells the *Smoke Gas-Analyser of Krell and Schultze*, which utilises the same principle in a different way. Of course these apparatus can also be used for any other gaseous mixtures, containing constituents of strongly different specific gravities.

Uehling and Steinhart (*Fischer's Jahresber.*, 1896, p. 1166) estimate CO_2 by the velocity of the gases issuing from a narrow orifice. Lux and Precht (*ibid.*, 1893, p. 1205) pass the gases through a hollow globe. Pfeiffer (Ger. P. 78612); Arndt (Ger. Ps. 70829, 125470, 129613); Dosch (*Z. für chem. Apparatenkunde*, 1907, p. 452), draw the gases through a receptacle, suspended from a balance. So does Siegert (*Z. Verein. deutsch. Ingen.*, 1888, p. 1090; 1893, p. 595), in whose apparatus the index of the balance indicates directly the percentage of carbon dioxide.

Another class of apparatus is that in which one of the gaseous constituents, mostly carbon dioxide, is *absorbed*, and the difference of volume before and after absorption is registered. These apparatus have the advantage of very easy registration, but the drawback that they act not continuously, but periodically, testing a sample of gas once about every five minutes and registering the result, as the gas must be left in contact with the absorbing agent for some little time. A definite volume of the gas to be tested is automatically drawn off, the carbon dioxide removed by soda-lime or caustic potash liquor, and the volume of the gas remaining after absorption is measured and registered.

The simplest apparatus of this class is that of Craig, in which between two synchronously running gas-meters a soda-lime absorbing apparatus is placed; the CO_2-percentage can be read off from the difference of the figures indicated by the indices of the meters (*Chem. Trade J.*, 1896, xviii. p. 445).

The apparatus of Arndt (Ger. Ps. 125470 and 160288; *Z. Verein. deutsch. Ingen.*, 1902, p. 320) is sold by the firm Ados, G.m.b.H., of Aachen, by the name of *Heat-effect-meter Ados.* It consists of a motor, moved by the chimney draught or by a water-jet pump, of the gas pumps and the absorbing apparatus with registering contrivance; it is shown in Fig. 99. The levelling bottle N, filled with glycerin, which is lifted by the motor, on descending aspirates laterally the smoke-gas to be tested. When it has arrived at its lowest position (shown in the figure), the gas-meter is just filled. If N is now raised, it forces a portion of the gas to be tested by D and E into the outer air, then closes the entrance channel for that gas, and, when arrived at the bottom end of E, shuts off exactly 100 c.c. in the gas-meter. By the further rising of the glycerin, the gas is forced into the absorbing vessel A, which is filled with caustic potash solution. The potash solution, displaced by the gas, rises into the space B, filled with air, and forces the quantity of air contained therein into the (nearly balanced) diving-bell K. This sets the registering apparatus GHJ into motion, and the position of the drum is marked on a slowly moving strip of paper. The less CO_2 there is in the gas, the more air will be displaced by the potash solution in the drum B, and the higher this drum will rise. When the levelling bottle N has arrived at the highest point, and the glycerin has risen up to the mark, a change of motion is automatically produced. Bottle N goes down, the glycerin goes back, the potash solution in the absorbing vessel A, the diving-bell K, and the liquor in the gas-reservoir return to their former position. The gas remaining after the absorption of the carbon dioxide is forced into the outer air by freshly aspirated smoke-gases. When bottle N has returned to the lowest position, a new test is beginning. If the absorbing space A is filled with *phosphorous* rods, in the place of potash

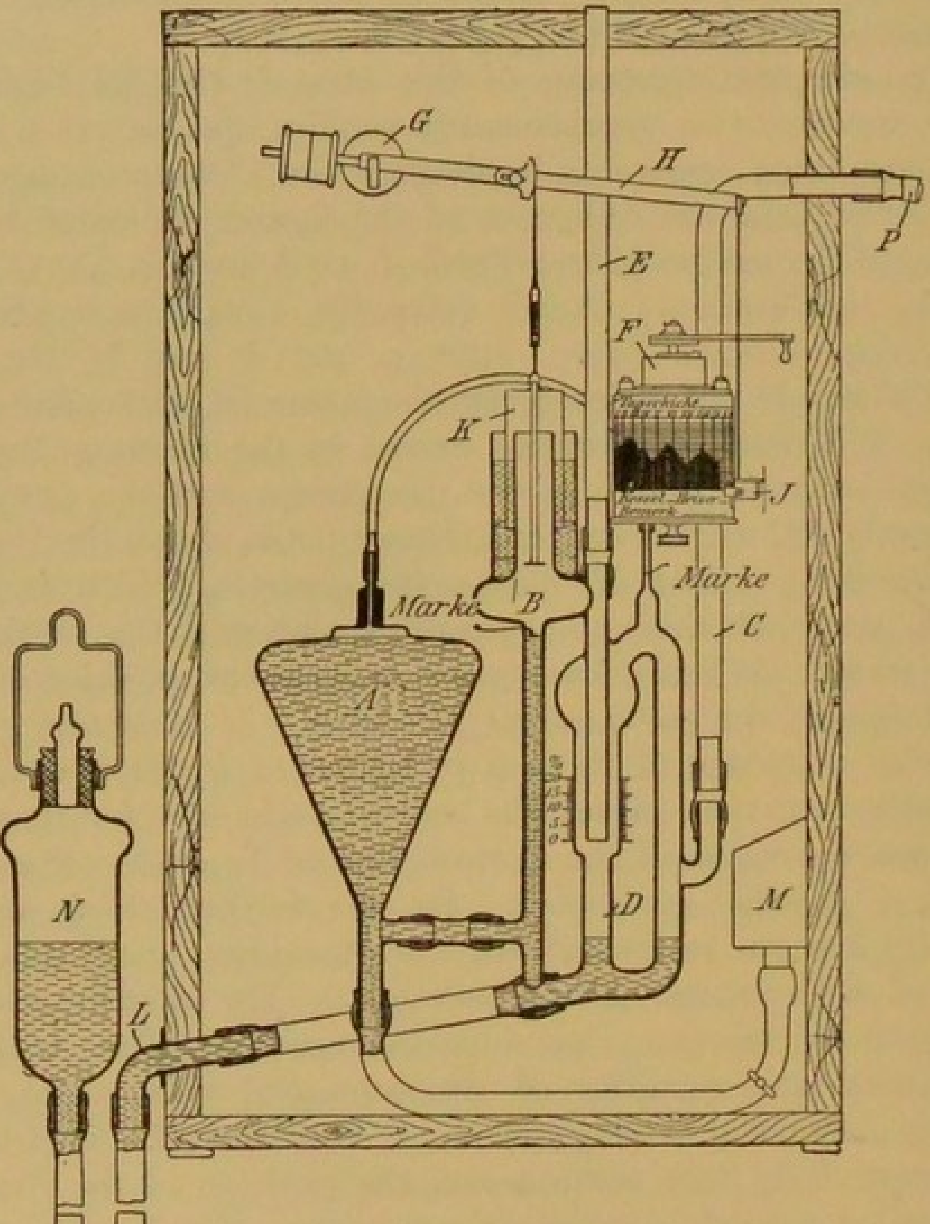


FIG. 99.

solution, the apparatus can serve for estimating the *oxygen* contents of the gases.

By improvements indicated in the Ger. P. 160288 (*Z. angew. Chem.*, 1905, p. 1231) it is possible to collect the gas always at atmospheric pressure, thus obviating the entrance of atmospheric air even when the gases are aspirated through the apparatus at reduced pressure.

The motor consists of a reservoir of liquid with a movable bell, which is almost entirely balanced by a counterweight. Below the bell is the aperture of a tube communicating with the chimney, provided with an air-valve which is turned by the movement of the bell itself, and thus causes the bell to go up and down. This movement is transferred by a cord and pulley to the gas-pumps and sets them into motion. These pumps are bells, diving in glycerin; when going up they aspirate gas, and when going down they force it into the absorbing apparatus. A controlling apparatus is described in their Ger. P. 238397 (*Z. angew. Chem.*, 1911, pp. 1233 and 2166).

On similar principles are founded the *Heat-effect-meter Monopol* (sold by Kurt Steinbock, of Frankfort-on-Maine) and the *Econograph* (manufactured by the Allgemeine Feuerungstechnische Gesellschaft, Wilhelmstrasse, Berlin W.).

The *Coometer of Schlatter and Deutsch* (made by Michael Pal & Co., London S.W., described by Samter in *Z. für chem. Apparatenkunde*, 1908, iii. 73) is made entirely of metal and makes four analyses per minute. The gas to be tested is aspirated by a pump, then forced by fine openings into the absorbing liquid, and thus the absorption very quickly produced. The unabsorbed gas acts upon an index which states directly the percentage of CO_2 on a visible disc.

Mertens (Amer. P. 1060996; *J. Ind. and Eng. Chem.*, 1913, p. 623) describes an automatic apparatus for measuring the percentage of carbon dioxide in furnace-gases by means of a Mariotté's bottle.

A further class of quickly working apparatus for continuous gas-testing is on the principle of introducing the gas into the apparatus by two conduits, in one of which the gaseous constituent to be estimated is removed, and its percentage is indicated by the *difference of pressure between the two gaseous currents.* On this is founded the *Autolysator* of Strache, Johoda, and Genzken (*Chem. Zeit.*, 1906, p. 1128; sold by the Verein. Fabriken für Laboratoriumsbedarf, in Berlin). Its principle is shown in Fig. 100. The gas is aspirated by a water-jet pump through a capillary tube, K_1, and by means of the regulating tap H the difference of pressure, measured by a differential pressure gauge, is kept uniform ; thus the quantity of air passing through K_1 during a minute is always the same. The same quantity of gas is also aspirated by a second capillary K_2, and between K_1 and K_2 the absorbing vessels A_1 and A_2 are interposed. When testing for CO_2, these vessels are filled with soda-lime. If there is no CO_2 in the gas, the differential pressure gauge M_2, attached to K_2, shows exactly the same as the gauge M_1; this is the zero point of the division. If there is CO_2 in the gas, it is retained in A_1 and A_2, and through K_2 now as much more gas must pass per minute as corresponds to the CO_2 present in the gas. Thereby the difference visible in the pressure gauge M_2 is increased, and the percentage of CO_2 can be read off directly on a scale. In the place of the regulating tap H an automatic regulator of the difference of pressure is employed, and the connecting pipes P_1 and P_2 can be provided with an apparatus, shown in Fig. 101, which automatically registers the differences of pressure occurring at K_2, and thereby the CO_2 percentage of the gas. Fig. 102 (p. 236) shows how the whole apparatus is arranged. The gas to be tested must be deprived of dust and moisture by filtration and drying, before entering into the apparatus. The advantages claimed for this apparatus are, first, rapidity of action (it indicates the composition of the gases every one to one and a half minutes); second, simplicity of construction and handling; third, insensibility against shocks and dirt; fourth, visibility of the diagram during the work, and from a distance.

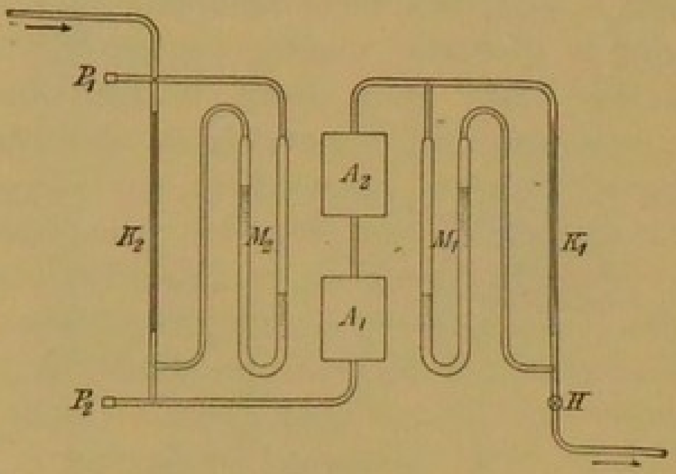


FIG. 100.

A new form of the "autolysator" is described in *J. Gasbeleucht.*, 1911, p. 548.

The apparatus of *Jones* (Amer. P. 854696; *Z. für chem. Apparatenkunde*, 1908, p. 124) is constructed on the same principle as the autolysator, but is less recommended than this.

Other apparatus for the same purpose have been constructed by the Drägerwerke (Ger. P. 236730; *Z. angew. Chem.*, 1911, p. 1646); Allgemeine Feuertechnische Gesellschaft (Ger. P. 228802; *ibid.*, p. 82); Arndt (Amer. P. 1065652; Ger. Ps. 231117, 232200, 233225; *ibid.*, pp. 468, 710, 801); Underfeed Stoker Co. (Ger. P. 233253; *ibid.*, p. 800); Knöll (Ger. P. 238503; *ibid.*, p. 2166); Hartung (Ger. Ps. 238398 and 244859; *ibid.*, pp. 2105 and 2266, and 1912, p. 1445); Wattebled (Ger. P. 234185; *ibid.*, p. 993); Arndt (Ger. Ps. 241074, 241075, 247165; *ibid.*, 1912, pp. 79, 80, 1445); Boulton (B. P. 5601 of 1912); Gaither (*J. Ind. Eng. Chem.*, iv. p. 611); Brubaker (*ibid.*, p. 599); E. Rupp (*Chem. Zeit.*, 1912, p. 59); A. Schmid (*Stahl u. Eisen*, 1912, xxxii. p. 245; *Chem. Zentralb.*, 1912, i. 967); H. M. Atkinson (*Chem. News*, 1912, cv. p. 136); Henderson and Russell (*Amer. J. Phys.*, 1912, xxix. p. 436; *Chem. Zentralb.*, 1912, i. p. 1860); Koenig (*J. Ind. Eng. Chem.*, 1912, vii. p. 844); the Uehling Instrument Co. (*Metall. Chem. Eng.*, x. p. 497).

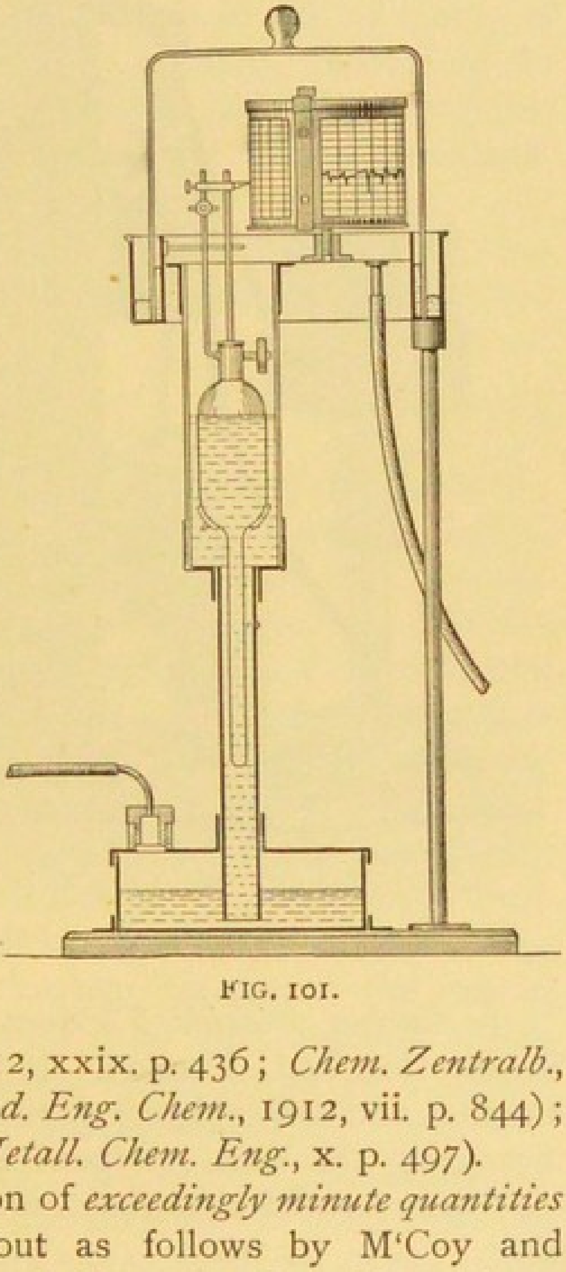


FIG. 101.

The detection and estimation of *exceedingly minute quantities of carbon dioxide* is carried out as follows by M'Coy and Tashiro (*8th Intern. Congr. Appl. Chem.*, i. 361; *Abstr. Amer. Chem. Soc.*, 1912, p. 3243). The minimum volume of gas required to produce an incipient reaction with 1 drop of barium hydrate solution is ascertained by means of a specially constructed glass bulb holding 25 c.c. The gas is introduced into this over mercury, and the volume of gas needed to render turbid a drop of baryta solution, protruding at the orifice of a tube laterally fused in the bulb, is measured by withdrawing mercury through the bottom tap. $1{\cdot}0 \times 10^{-7}$ g. of CO_2 could be detected in this way.

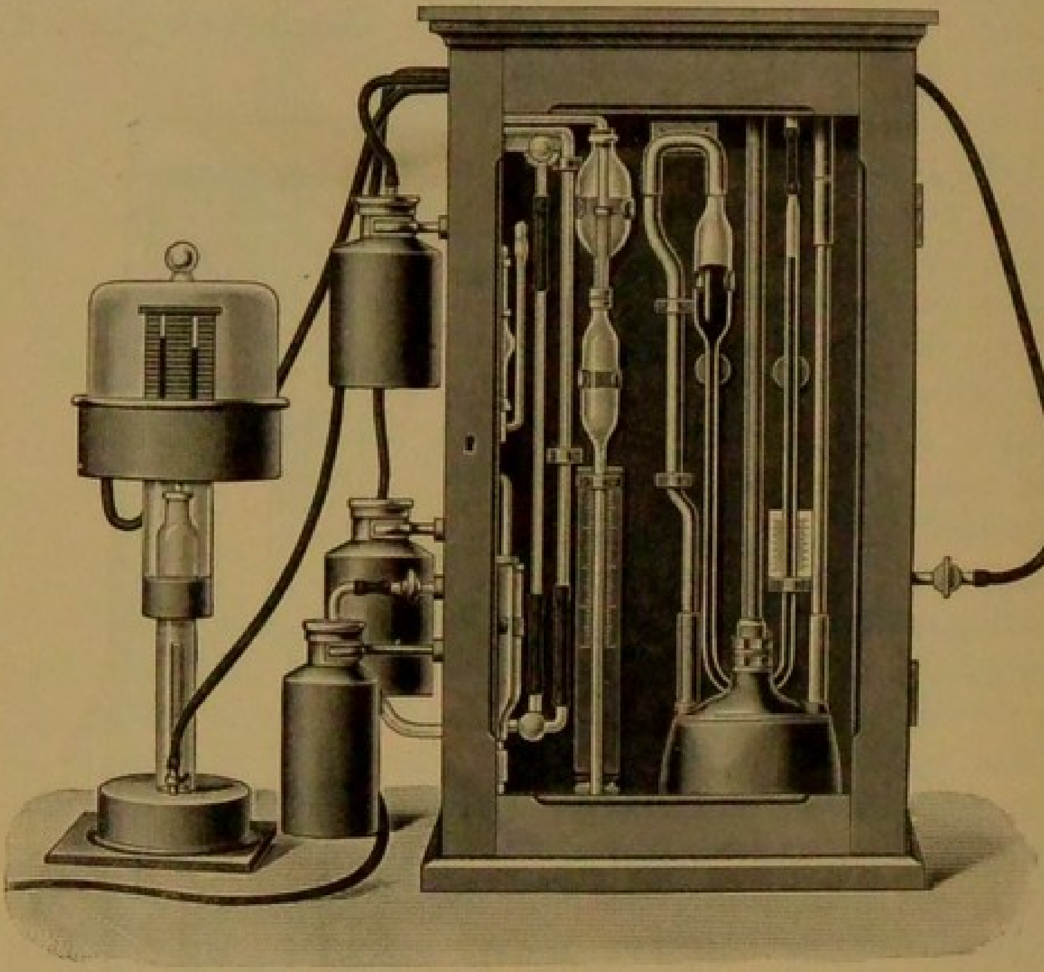


FIG. 102.

A *Carbon Dioxide Thermoscope* is sold by the Underfeed Stoker Co., Ltd., London. It is a small thermoscope, easily handled and self-registering, which detects the CO_2 in a gas by measuring the heat produced by the action of CO_2 on solid caustic, and registers the percentage directly on the thermoscope scale.

Optical methods for the testing of fire-gases, etc., for carbon dioxide. The *Refractometer* of Haber has been already described on p. 176.

Measurement of the Heat produced by the Absorption of Carbon Dioxide by the Absorbing Reagent.—Apparatus for this purpose has been described by Hinmann (Ger. P. 228784; *Z. angew. Chem.*, 1911, p. 83, and 1912, p. 1422); Müller (Ger. P. 233463; *Z. angew. Chem.*, 1911, p. 899, and 1912, p. 1422).

The estimation of *carbon dioxide in technical chlorine* is described later on in the chapter dealing with chlorine.

The estimation of carbon dioxide dissolved in water is treated upon by L. W. Winkler (*Z. anal. Chem.*, xlii. p. 735; *Chem. Zentralb.*, 1904, i. p. 608), who drives it out by means of hydrogen and absorbs it in caustic potash. According to Casares and Pina de Rubies (*Chem. Zentralb.*, 1913, i. p. 2177) this method is unreliable if small quantities are to be determined, the deviations amounting to 4 mg.

Tillmans (*J. Gasbeleucht.*, 1913, pp. 348 and 370) has examined the various methods for estimating CO_2 dissolved in water.

Carbon Monoxide.

Qualitative detection of traces of carbon monoxide in the air of heated rooms, coal-pits, etc. (*Cf.* on this subject Lunge-Keane's *Technical Methods of Chemical Analysis*, vol i. pp. 889 *et seq.*) If blood is diluted with water so far that the mixture shows only a just perceptible pink shade, it gives a characteristic absorption spectrum, showing two dark bands between the lines D and E. If to this dilute blood solution a few drops of strong, recently prepared ammonium sulphide are added, those black bands vanish, and are replaced by a single broad band, lying between the two above-mentioned bands. Quite different from this is the behaviour of blood containing carbon monoxide. To begin with, in the presence of carbon monoxide the scarlet colour of blood changes into pink, and this solution yields almost exactly the same absorption spectrum as pure blood; *but the two bands do not vanish on adding ammonium sulphide.*

H. W. Vogel (as reported in Treadwell's *Lehrb. d. analyt. Chemie*, ii. p. 542) carries this method out in the following way:—A 100 c.c. bottle, filled with water, is placed in the room, the air of which is to be tested for CO; 2 or 3 c.c. of a very dilute solution of blood, which in the thickness of the layer contained in a test-tube shows the blood spectrum, is put into the bottle which is closed and shaken ; a few drops of ammonium sulphide are added, and the liquid is observed in the spectroscope. If the two bands do not vanish, carbon monoxide is present. According to Vogel up to 0·25 per cent. CO can be proved in this way. According to Czakó (*Beiträge zur Kenntnis naturlicher Gasausströmungen*, 1913, p. 24) the air to be tested for CO by this method should be first purified from oxygen by means of phosphorus or sodium hydrosulphite.

Hempel (*ibid.*, p. 542) has greatly improved this method by passing the gas through two funnels, connected by an india-rubber ring, after placing a mouse into the space thus formed. The gas is passed through this contrivance during three or four hours at the rate of 10 litres per hour. The mouse is then killed by immersing the funnels in water, and a few drops of its blood are taken out near its heart, which are diluted with water and spectroscopically tested as described above. In this way Hempel succeeded in proving with certainty down to 0·032 per cent. CO. If there is too little CO present, no visible symptoms of poisoning can be observed ; these appear only if the amount of CO is 0·06 per cent., after half an hour. The mouse then exhibited dyspnœa and lay on one side.

Potain and Drouain (*Compt. rend.*, cxxvi. p. 938) prove the presence of small quantities of carbon monoxide by passing the gas through a very dilute solution of palladium protochloride, whereby metallic palladium is separated:—

$$PdCl_2 + CO + H_2O = 2HCl + CO_2 + Pd.$$

The solution is decolorised by larger quantities of CO, or assumes a faint grey colour, but in the presence of mere traces it is light yellow. In order to observe the colour more distinctly, they filter it from the separated palladium, and compare its colour with that of the original platinum solution.

Nowicki (*Chem. Zeit.*, xxxv. p. 1120; *Z. angew. Chem.*, 1912, p. 231) utilises the same method for a small portable apparatus, containing a strip of paper moistened with palladium protochloride solution, the blackening of which indicates the presence of CO. The volume per cent. CO and the time in minutes up to complete blackening are respectively 0·010—11.60; 0·25—5.32; 0·050—3.16; 0·075—2.12; 0·100—1.9; 0·250—11/15; 0·500—13/30; 1·000—4/15.

Cl. Winkler (*Z. anal. Chem.*, 1889, p. 267) describes a colorimetrical test for CO. The gas is treated with a solution of 100 g. cupric chloride in 1 litre of nearly saturated sodium chloride solution. This solution is colourless or but slightly brownish; in contact with air it forms a green precipitate of cupric oxychloride, but it keeps unchanged in a bottle closed by a rubber cork, and provided with a copper spiral reaching from top to bottom. If the gas to be examined is passed through this solution, or agitated with it in a closed bottle for some little time, most of the CO is absorbed. A portion of the liquid is put into a test-tube, where it is diluted with three or four times its volume of water, without troubling about the white precipitate of cuprous chloride (this is indispensable); then a drop of a solution of sodium palladium protochloride is added. In the presence of the slightest quantity of carbon monoxide a black cloud of finely divided palladium is formed. If the test is always performed under exactly similar conditions, the depth of the black colour admits of approximately guessing at the quantity of carbon monoxide. Thus 0·01 c.c. CO = 0·0000125 g. can be found. The presence of other gases does not materially influence the reliability or sensitiveness of this reaction. (Treadwell, in his *Lehrb. der anal. Chem.*, 3rd ed., vol. ii. p. 543, declares this test to be wrong, because, as he convinced himself, a black precipitate of metallic palladium is formed also in the absence of carbon monoxide, since cuprous chloride by itself easily reduces dilute palladium salts to metallic palladium.)

We must also refer to the testing of air for inflammable gases generally, described in a subsequent chapter, which, of course, will indicate carbon monoxide as well.

Quantitative Estimation of Carbon Monoxide.—The usual way of estimating this gas is by absorption in an ammoniacal or acid solution of cuprous chloride (*suprà*, p. 126 *et seq.*) by means of a Hempel pipette (p. 89) or a Bunte burette, as described pp. 64 *et seq.* The combustion method can also be employed (p. 109). L. A. Levy (*J. Soc. Chem. Ind.*, 1911, p. 1437) discusses the estimation of this gas. According to him the cuprous chloride method neither gives a sharp reaction, nor does it indicate small percentages. A number of colorimetric methods has been described for the estimation of CO, but they are not sufficiently simple and accurate for industrial purposes. Winkler (*Z. anal. Chem.*, 1889, *vide suprà*) employs for this purpose the black cloud of reduced palladium formed by shaking up the gas with palladium chloride and cuprous chloride. Potain and Drouin (*Comptes rend.*, cxxvi. p. 938) employ the progressive loss of colour experienced by palladium chloride solution on reduction by carbon monoxide. Others employ the change of colour exhibited by dilute blood solution and the reduction of ammoniacal silver oxide. Levy himself tried gold chloride (recommended by Donau, *Akad. der Wiss. Wien*, cxiv. p. 79), but not with good results, as he explains in detail. Ultimately he adopted the method of Gautier and Clausmann (*Comptes rend.*, cxxvi. p. 793; *vide suprà*, p. 127), the selective oxidation of carbon monoxide by heated *iodine pentoxide*, and observing the iodine liberated, from which he developed the following method:—The carbon monoxide is selectively oxidised to carbon dioxide, and the oxidised gas is aspirated through a fixed volume of standard baryta solution coloured by phenolphthalein, until the solution is decolorised by the saturation of the baryta, which corresponds to a fixed volume of carbon dioxide, or the same fixed volume of CO oxidised into CO_2. An observation of the volume of gas required to effect this decolorisation indicates the percentage of CO. The following points must be observed:—Unsaturated hydrocarbons, which are oxidised by iodine pentoxide, must be first removed, probably by a strong solution of bromine in potassium bromide, followed by a treatment with strong caustic potash solution, which also absorbs any CO_2 originally present in the gas; then drying the gas by passing it over phosphorus pentoxide in a tube 1 in. in diameter and 4 in. long (which for various reasons is preferable to strong sulphuric acid); then passing the gas through iodine pentoxide, mixed with small pieces of ignited asbestos, contained in a U-tube, which is fused to another tube containing copper turnings for retaining the iodine liberated from the pentoxide by the CO, this compound U-tube being placed in an air-oven maintained at 168° to 180° C. The gas now enters into the "decolorisation vessel" containing the baryta solution. This vessel (supplied by Messrs Alexander Wright & Co., Ltd., Westminster) is similar to a Winkler coil (p. 145), but the slopes are considerably steeper. The baryta solution employed here is of such a strength that it is neutralised by the passage of 20 c.c. carbon dioxide measured at 60° F. and 30 in. pressure. A three-way tap is interposed before the last vessel, so that the gas may be bye-passed until the commencement of a test. The gas is drawn through the apparatus by the flow of water from an aspirator, the volume of the outflowing water being equal to the total volume of gas passing through. If this volume is called V c.c., then as 20 c.c. of carbon monoxide is contained therein, the percentage of the latter is $= \frac{2000}{V}$. For practical use the aspirator is graduated directly in percentages of carbon monoxide. Experiments quoted in the paper showed that the colorimetrical results obtained with gases of high carbon monoxide content agreed within about 0·3 per cent. with analyses made by the most accurate methods.

When the gas contains but little CO, a more dilute baryta solution must be used, but the absorption in this case is not quite complete. For the purpose of getting accurate results with gases containing only traces of CO, *e.g.* fumes from gas-stoves, air from pits or lime-kilns, etc., the gas is drawn by means of a filter-pump through a meter and then through the apparatus. A strong baryta solution is employed. After a certain time the pump is stopped and the excess of baryta back-titrated with oxalic acid. In the discussion on this paper, reported *loc. cit.*, several speakers expressed doubt whether this method would answer in the hands of unskilled persons.

If the gas remaining after the estimation of carbon monoxide and removing aqueous vapour and carbon chloride is passed through a combustion tube 60 cm. long, half filled with cupric oxide and half with platinum asbestos, and heated to a dark red heat, hydrogen and methane are completely burnt to water and carbon dioxide, which are collected as above, and from which the H_2 and the CH_4 are calculated.

Burrell (*Science*, xxxv. p. 423) describes an apparatus for this purpose.

Haldane (*J. Ind. and Eng. Chem.*, 1910, p. 9) describes a colorimetric method for the determination of CO in air, founded on the formation of oxyhæmoglobin in a blood solution.

Haldane (*The Investigation of Mine Air*, by Forster and Haldane, pp. 100 and 115) also describes special apparatus for the analysis of mine air, both in the laboratory and *in situ*.

Other publications on the determination of carbon monoxide are:—

Pontag (*Z. Unters. Nahr. u. Genussm.*, 1903, 674).

Spitta (*Arch. f. Hygiene*, xlvi. p. 287; *J. Soc. Chem. Ind.*, 1903, p. 652).

Gautier (*ibid.*, 1898, p. 931; *J. Gas Lighting*, cxxi. p. 547).

Kinnicutt and Sandford (*J. Amer. Chem. Soc.*, 1900, p. 14).

Nesmjelow (*Z. anal. Chem.*, 1909, p. 232).

Worrell (*Met. Chem. Eng.*, 1913, xi. p. 245).

Sinnat and Cramer (*The Analyst*, 1914, p. 163).

Seidell (*J. Ind. and Eng. Chem.*, 1914, p. 321).

Brunck (*Z. angew. Chem.*, 1912, p. 2479) employs the reaction, utilised by Winkler (*suprà*, p. 240) for the qualitative discovery of carbon monoxide, in the following manner for the quantitative estimation of small quantities of it in gaseous mixtures. Since the hydrogen chloride, formed by the reaction, $CO+PdCl_2+H_2O=CO_2+Pd+2HCl$, in the presence of oxygen oxidises a little of the reduced metal, this disturbing reaction is avoided by the addition of sodium acetate; the free acetic acid now formed does not act upon the metal. He employs a gas-normal solution of sodium palladium chloride, containing per litre 4·762 g. palladium, 1 c.c. of which corresponds to 1 c.c. of CO at 0° and 760 mm. pressure. The sodium acetate is used in the shape of a 5 per cent. solution, of which about half of the volume of the palladium solution is used. The apparatus is extremely simple, and consists of an Erlenmayer flask closed by a twice perforated rubber cork, the perforations being closed by glass rods ending in bulbs. In that place of the neck to which the cork descends, a mark is made, and the contents of the flask (0·5 to 2 litres) up to this mark are ascertained. The flask is filled with the gas to be examined, either over water or in the dry way, after replacing the glass rods by glass pipes, which in the end are quickly drawn out so that the rods can be put in. In the same way the solutions, first that of palladium and then that of the sodium acetate, are introduced; the volume of these solutions is deducted from the contents of the flask. The reaction, which is assisted by occasional shaking, is finished in at most an hour. If the liquid has remained clear, no CO has been present. Otherwise the precipitated palladium is collected on a small filter, washed with hot water, dried, and the filter is burnt and the remaining palladium heated in a current of hydrogen for a short time. One g. of Pd answers to 0·2624 g. CO = 210 c.c. at 0° and 760 mm. This method yields very good results, but it is not applicable in the presence of hydrogen or unsaturated hydrocarbons, which equally reduce the palladium compounds.

L. A. Levy (B. P. 12841 of 1911; *J. Gas Lighting*, cxxii. pp. 455 and 515) estimates the carbon monoxide colorimetrically, by utilising the observation of Donau, that a solution of gold chloride, reduced by carbon monoxide, yields a colloidal solution of gold of a ruby colour. He passes a certain quantity of the gas through a gold solution and then compares the colour with that of a standard solution.

Nicloux (*Bull. Soc. Chim.* [4], xiii. p. 947) describes an apparatus for extracting the carbon monoxide from blood without the aid of a mercurial pump (abstr. in *Chem. Zeit.*, 1912, ii., p. 1838).

SULPHUR DIOXIDE.

We have already described the estimation of this gas by the apparatus of Hesse (p. 135), of Reich (p. 137), of Lunge and Zeckendorff (p. 142), of Ost and of Wislicenus (p. 150), etc., etc.

We shall now describe special methods proposed for this purpose.

Seidell and Meserve (*J. Ind. and Eng. Chem.*, 1914, p. 298) estimate sulphur dioxide in air by titration with iodine.

Ljungh (*Chem. Zeit.*, 1909, p. 143) employs a modification of Reich's apparatus, by which any required corrections of pressure can be carried out in a very simple way. The outlet tube *b* of the bottle B, Fig. 103, is connected by a thick-walled rubber tube with the tap *i*, which is fixed by a clamp at the perpendicular brass rod *s*, so that it can be adjusted to the changing level of water in B. The manipulation is similar to that with Reich's apparatus. Tap *h* makes connection with the gas containing SO_2; bottle A receives a measured volume of decinormal iodine solution, say 10 c.c. After closing it, tap *i* is opened and the point of rod *s* is put on the same height as the water-level in B. Now *h* is opened, so that the gas passes through *a* into A; the non-absorbed gas goes into B, and the water displaced by it is collected. At the moment when the iodine solution A is decolorised, *h* is closed, and soon after the flow of water from B ceases. Now point *s* is again placed on a level with the water in B, whereby a little water is made to run off, and the volume of the water displaced is measured. The calculation of the results is made just as in the case of the Reich-Lunge apparatus shown *suprà*, p. 138.

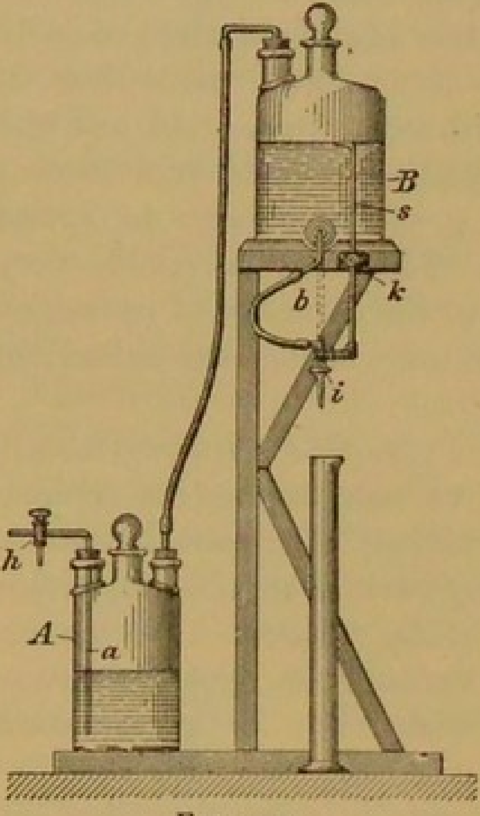


FIG. 103.

Estimation of Sulphur Dioxide in the Presence of Nitrous Vapours, e.g. *in the Gases of Vitriol-chambers.*—In presence of sensible quantities of nitrous acid, Reich's method and its congeners are not directly applicable; too much gas is then used for the test, and its percentage of SO_2 is therefore underestimated. This is caused by the fact that the HJ formed by the reaction is reduced to J by the nitrous acid. To avoid this, Raschig (*Z. angew. Chem.*, 1909, p. 1182) adds to the ordinary charge of Reich's apparatus (consisting of 10 c.c. decinormal iodine solution, 100 c.c. water, and a little starch solution) 10 c.c. of a cold saturated solution of sodium acetate. The test is carried out in the usual manner, as described, p. 137, but the gases are passed through a tube containing glass-wool, in order to prevent any droplets of sulphuric acid getting into the iodine solution. In this case there is no "after-blueing," as sodium nitrite and sodium sulphite do not act upon each other. This method admits of estimating the *nitrous gases* as well, by adding, after the estimation of SO_2, a drop of phenolphthalein to the decolorised liquid, and titrating with decinormal caustic alkali till a red colour appears. From the cubic centimetres of decinormal alkali 10 c.c. must be deducted for the HJ formed, and 10 c.c. for the H_2SO_4 formed according to the equation given *suprà*, p. 140. The excess of decinormal alkali over and above this 20 c.c. indicates the nitrous or nitric acid present.

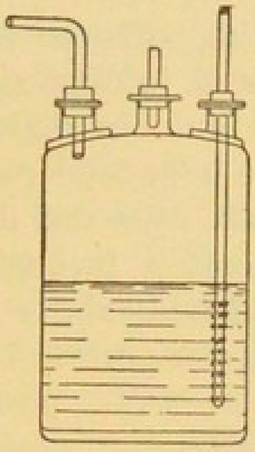


FIG. 104.

For the *estimation of total acids*, $SO_2 + SO_3$ (*cf.* above, p. 141), Lunge recommends the bottle shown in Fig. 104. The inlet-tube is closed at the bottom and the portion immersed in the solution pierced by a number of small holes, whereby the stream of gas is subdivided. This bottle is also employed for estimation of SO_2.

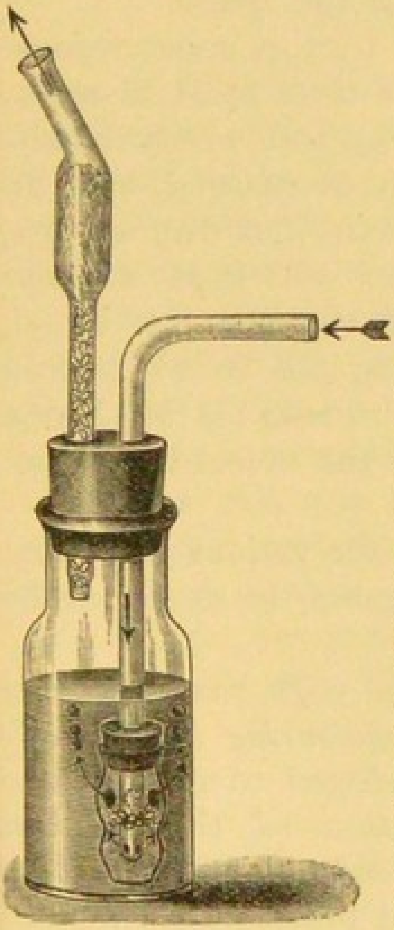


FIG. 105.

Fig. 105 shows the absorption flask employed by the English alkali inspectors (34*th Report*, *for* 1897, p. 22), which gives good results even in the most difficult cases, *e.g.* in the absorption of acid fog. It cannot be used for iodine solution, on account of the rubber stopper, but it is very suitable for the just-mentioned Lunge test, also for the absorption of hydrochloric acid, and in many other cases. The figure shows the apparatus in half the actual size. It is a flask fitted with a rubber stopper provided with an inlet- and an exit-tube as shown. The former is 8 mm. wide, closed at the bottom and pierced with a number of small holes, through which the gas passes to the double bulb, which is attached to the tube by a rubber stopper. The upper bulb is filled with small cuttings of rubber tubing, kept in motion by the stream of gas, which is thus brought into very intimate contact with the absorbing solution; the lower bulb is open at the bottom. The success of the apparatus depends largely on the correct dimensions being adhered to. The lower opening of the double bulb is 6 mm. in diameter, the lower bulb 15 mm. and the upper bulb 18 mm. in diameter, and the upper opening, through which the inlet-tube passes, 13 mm. wide. The gas passes from the bulb into the flask through several small holes, and finally leaves it through the exit-tube, which is narrowed below and widened above to form a cylindrical chamber; the lower, narrow portion is filled with rubber rings, and the upper, wider portion with glass-wool. When used for the absorption of acid vapours, the exit-tube is moistened with water coloured by methyl orange, which serves to indicate whether complete absorption is being effected in the bottle.

Henz (*Z. angew. Chem.*, 1905, p. 2002) recommends for the estimation of total acids in waste gases the vessel shown in Fig. 106, which is half-filled with glass beads. It is charged with 25 c.c. standard alkali; a certain quantity of gas, measured by running water off from a large stoneware pot, is aspirated through this vessel, the contents (without rinsing the vessel) poured into a beaker and titrated with acid till the change of colour is produced, poured back into the vessel, blown out into the beaker, and the titration finished.

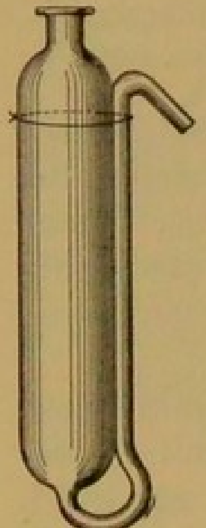


FIG. 106.

Of course for the purpose in question the various absorbing apparatus specially intended for poor gases, as described on pp. 145 *et seq.*, can be employed.

Lunge (*Z. angew. Chem.*, 1890, p. 567) has suggested determining the *acidity of kiln-gases by measuring their specific gravity*, a method which might be developed to give a continuous graphic record of the operation of the furnace. Difference of 1 per cent. of sulphur dioxide by volume affect the specific gravity in the second decimal place. Such modifications might be made by a modification of the Lux gas-balance (*suprà*, p 183), which, however, as at present constructed is not suitable for use with acid gases, or by the aid of F. C. Müller's method of determining the density of gases (*ibid.*, p. 513). The "Ados" apparatus (p. 231) or the "Autolysator" (p. 233) might also be employed. This proposal does not seem to have been worked out in practice.

The *electric conductivity* of aqueous solutions of sulphur dioxide is employed for estimating the SO_2 in the air by Kullgren (*J. Chem. Soc. Abstr.*, vol. civ. p. 525).

Estimation of Sulphur Dioxide and Sulphur Trioxide alongside of each other, e.g. in roaster-gases catalysed by platinum.

Bodenstein and Pöhl (*Z. Electrochem.*, 1905, p. 378) pass such gases into a measured quantity of iodine solution, retitrate the remaining free iodine with thiosulphate solution, and thus obtain the quantity of SO_2 not converted into SO_3. By titrating the decolorised solution with baryta solution they determine the total acidity, which is partly due to the SO_3 formed by catalysis, and partly to the acids formed by the reaction:

$$SO_2 + I_2 + 2H_2O = 2HI + H_2SO_4.$$

Eugene Richter (*Z. angew. Chem.*, 1913, 132) has not obtained satisfactory results by this method; he prefers condensing the SO_3 by cooling the gases down to ordinary temperature, dissolving the SO_3 in water, and precipitating the sulphuric acid formed by barium chloride.

Kastle and McHargue (*Amer. Chem. J.*, 1907, p. 38; *Chem. News*, xcvi. p. 237) proceed in a similar way, but they determine the total acidity by titration with decinormal sodium hydrate solution and phenolphthalein.

If we call the cubic centimetres of decinormal iodine consumed a, and the cubic centimetres of decinormal causti soda (or baryta) b, the quantity (in grammes) of unchanged $SO_2 = x$ is 0·003204 a, and that of the SO_3 formed $y =$ 0·004004 $(b-2a)$. The percentage yield of SO_3 is:

$$\frac{(b-2a) \times 100}{b-a}.$$

Ljungh (*Chem. Zeit.*, 1909, p. 143) prescribes estimating the loss of SO_3 in the exit-gases from making SO_3 by contact processes by aspirating a slow current of gas through a measured quantity of seminormal caustic soda, retitrating the unconsumed soda with normal acid and methyl orange, and running the liquid, diluted up to a certain volume, into a measured volume of 1/100 normal iodine, to which a little starch has been added, up to decolorisation. We abstain from quoting his way of calculating the result, as the process is quite faulty, since the absorption of SO_2 by caustic soda in the presence of oxygen causes the formation of much sulphuric acid, and thus makes the results of converting the SO_2 into SO_3 appear too favourable.

Hawley (*Eng. and Min. J.*, xciv., p. 987) avoids the errors connected with indirect methods by filtering the SO_3 out from the SO_2 and then determining it. The gas is drawn through two glass funnels, which are connected together with their large ends. Between the funnels a sheet of moist filter-paper is inserted on which the SO_3 is condensed. At the end of the process the SO_3 is washed into a beaker and titrated with decinormal soda solution and methyl orange.

SULPHURETTED HYDROGEN (HYDROGEN SULPHIDE).

Detection.—This is especially important in the manufacture and control of illuminating gas. The purified gas, as it goes in the street mains to the consumers, ought to be completely free from H_2S. In order to ascertain this, a large quantity, say 1000 litres of street-gas, is carried over lead-paper, moistened with water or dilute liquor ammoniæ, which is blackened by the formation of PbS. If this happens after all, and a quantitative estimation is required, the volumetric absorption by cadmium chloride in any one of the well-known apparatus (Hempel, Bunte, etc.), or else the following method, can be applied.

Ganassini (*Boll. chim. farm.*, 1902, p. 417) employs for the detection of H_2S its reaction with ammonium molybdate. The reagent is prepared by dissolving, on the one hand, 1·25 g. of ammonium molybdate in 50 c.c. of water, on the other hand 2·5 g. potassium sulphocyanate in 45 c.c. of water, mixing these two solutions and acidifying with 5 c.c. of concentrated hydrochloric acid. The solution is stable for some days, if kept in a stoppered bottle and protected from the light. It is employed by moistening the inside of a small porcelain dish and allowing the gas to impinge upon it; or by dipping a piece of filter-paper into the reagent and holding this in the gas. If hydrogen sulphide is present, a more or less interior pink colour is produced, which is not the case with acetylene or sulphur dioxide.

Quantitative Estimation.—In *crude* coal-gas sulphuretted hydrogen is always present up to 1 per cent. by volume, and it is just one of the principal objects of purifying the gas to remove the H_2S by ferric hydroxide, lime, etc. Therefore its quantity in crude gas must be determined, for which purpose the following methods are employed:—

1. *Gravimetric Estimation.*—Fresenius (*Quant. Analysis*, 7th ed., vol. i. p. 383) employs as absorbent pumice-stone saturated with cupric sulphate. The absorbent is prepared by pouring over 60 g. pumice, in pieces of the size of a pea, a solution of 30 g. cupric sulphate, evaporating to dryness, while stirring the mass, and heating to 150° for four hours. A U-tube is filled with this mass for five-sixths of its length, the last sixth being filled with dry calcium chloride. The crude gas must be completely purified from tar by means of a large drying cylinder filled with cotton-wool; after this comes another absorbing bottle, filled with moistened vitreous phosphoric acid for retaining any traces of ammonia, and a calcium chloride tower for completely drying the gas. This is now passed through a tared U-tube, filled with the copper-sulphate pumice, where the H_2S is retained (it is best to use two such U-tubes in succession), which is indicated directly by the increase of weight. At last comes a gas meter for ascertaining the quantity of gas examined. When testing street-gas, at least 1 cb.m. must be employed; for crude gas much less is sufficient. At the end, dry air is drawn through the apparatus. Each gramme increase of weight of copper-sulphate pumice indicates 681·3 c.c. H_2S at 15° and 760 mm., when saturated with moisture.

According to L. T. Wright (*J. Soc. Chem. Ind.*, 1885, p. 665) a more suitable absorbent for H_2S is the cupric phosphate obtained by precipitating a solution of cupric sulphate with sodium hydrogen phosphate. This reagent is prepared by adding a solution of 100 g. of crystallised sodium hydrogen phosphate to 500 c.c. water, with constant stirring, to a solution of 125 g. of crystallised cupric sulphate in 750 c.c. water, filtering off the precipitated copper phosphate, and drying it at 100°. It is employed in a U-tube, one-sixth of which is filled with calcium chloride, just like the cupric sulphate.

E. P. Harding and Einer Johnson (*J. Ind. and Eng. Chem.*, 1913, p. 836) employ for the estimation of H_2S in coal-gas cadmium chloride, either gravimetrically or volumetrically. According to E. Johnson's Amer. P. No. 1074795, the gas is passed through a solution of cadmium which retains the H_2S, the other gases escaping. From the absorbing agent the H_2S is liberated by treating it with HCl *in vacuo*, and titrating the H_2S under reduced pressure. The patent shows apparatus for carrying out this method.

2. *Volumetric Estimation.*—According to Bunte (*J. Gasbeleucht.*, 1888, p. 899; confirmed by Kast and Behrend, *ibid.*, 1889, p. 159) this is best performed by Dupasquier's method, viz., by a standard solution of iodine in potassium iodide, by the reaction $H_2S+I_2=2HI+S_2$. The solution employed contains 1·0526 g. iodine per litre, 1 c.c. of which indicates 0·1 c.c. of H_2S, measured moist at 15° and 760 mm. The gas to be tested, after being freed from tar-fog and ammonia, is passed into a completely dry Bunte burette (if necessary, with the assistance of an aspirator) and a portion of the gas then sucked out to make room for the reagents. The iodine solution is then sucked in from a small dish so as to fill the capillary and bore of the stopcock, and then starch solution to the lowest division mark (−10). By gradually adding fresh quantities of iodine and repeated shaking, the end-point of the reaction is recognised by the appearance of a permanent blue colour. The amount of iodine used is read off directly on the burette, the amount remaining in the capillary being balanced by that added before the starch, which is not measured. The volume of gas used is then determined in the usual manner.

An alternative method consists in employing a dry bottle of known capacity (about 500 c.c.), closed with a hollow stopper capable of holding 25 c.c. (A glass tube of this capacity, closed at one end and fitted into a rubber cork, the bottom of which is coated with a film of paraffin wax, may be substituted for a ground-in stopper.) The gas, purified from tar and ammonia, is blown through the inverted bottle till all air is driven out. The tube or stopper, into which 25 c.c. of decinormal iodine solution has been placed, is inserted while the bottle is still inverted, and the solution shaken with the gas; the contents of the bottle and stopper are then washed out, and the excess of iodine determined by titration with sodium thiosulphate and starch. Each cubic centimetre of iodine solution equals 1·122 c.c. of dry H_2S at 0° and 760 mm.; the percentage of the gas is calculated in exactly the same manner as indicated for carbon dioxide on p. 227, with the substitution of the figure 1·108 for that of 1·119 in the equation.

The iodine method is liable to give high results, since the unsaturated carbon compounds and also hydrocyanic acid equally tend to combine with iodine. In the case of coal-gas the error thus caused is usually small, but it is very considerable in the case of oil-gas and of carburetted water-gas, owing to the presence of cyclopentadien, C_5H_6 (Ross and Race, *J. Soc. Chem. Ind.*, 1910, p. 604).

Somerville (*J. Gas Lighting*, 1910, p. 29) describes a modified iodometric method in which the gas is drawn by means of an aspirator through a wash-bottle of 100 c.c. capacity, containing 10 c.c. of *N*/1000 iodine solution and 10 c.c. of specially prepared starch solution, diluted to 100 c.c. The passage of the gas is continued until the blue coloration just disappears, the volume of gas used being found from the volume of gas run off from the aspirator. To obviate the error due to the above-mentioned impurities, a second test is made with the same gas, which is first passed through a small tower containing lead carbonate to remove the sulphuretted hydrogen; by deducting the second results from the first, the true amount of H_2S is found.

3. *Colorimetric Estimation.*—Vernon Harcourt (Lunge-Keane's *Technical Methods*, etc., vol. ii. p. 667) employs this method, especially in cases where sulphuretted hydrogen is only present in small quantities. The gas is bubbled in a fine stream through a standard-sized tube containing a solution of lead oxide in an excess of sodium hydroxide, with addition of sugar. The passage of the gas is continued until the solution attains the same brown colour as a similar-sized standard tube, which is artificially made to correspond with the colour given to the standard lead solution by 0·0025 grains (0·000162 g.) of sulphur, by mixing solutions of copper,

cobalt, and ferric sulphates. The gas is drawn through the solution by an aspirator, the water run out being collected in a measuring cylinder and thus indicating the volume of gas passed through. The brown solution becomes colourless on exposure to light, and provided that carbon dioxide is excluded, the revivified solution may be used over again for a considerable number of times.

L. W. Winkler (*Z. anal. Chem.*, 1913, p. 641) estimates the hydrogen sulphide in natural waters colorimetrically by means of an ammoniacal solution of arsenic trisulphide.

Estimation of Sulphur Dioxide and Sulphuretted Hydrogen in presence of each other.

These gases cannot coexist to any considerable extent, owing to the reaction $SO_2 + 2H_2S = 2H_2O + 3S$, but they may occur together in very small quantities, *e.g.* in the exit-gases from the Claus kilns. For the *qualitative* proof of the presence of SO_2 in the presence of H_2S, Votocek (*Ber.*, 1907, xl. p. 414) recommends a solution, prepared by mixing 3 vols. of a solution of 0·25 g. fuchsin (magenta) in 1000 c.c. water and 1 vol. of a solution of 0·25 g. malachite-green, in 1000 c.c. water. The gas to be tested is passed through a U-tube containing a hot solution of cadmium sulphate, then through a U-tube containing the above solution, to which a little sodium bicarbonate has been added. If the reagent is decolorised and if on addition of acetaldehyde a purple colour is produced, sulphur dioxide has been present.

The *quantitative* estimation of such a mixture is founded on the fact that, whilst both H_2S and SO_2 in contact with iodine form 2 molecules of HI for each atom of sulphur present, the H_2S does not give any further increase in the acidity, but the SO_2 gives rise to an equivalent of sulphuric acid ; thus:

$$H_2S + I_2 = 2HI + S.$$

$$SO_2 + I_2 + 2H_2O = 2HI + H_2SO_4.$$

The sum of H_2S and SO_2 is measured by estimating the quantity of iodine converted into HI and the SO_2 by the determination of the acidity remaining after the HI thus formed has been neutralised. Since, however, the passage of a large volume of gas through iodine solution volatilises a portion of the iodine, it is necessary to insert a flask containing sodium hydroxide, or, preferably, sodium thiosulphate solution. One or more litres of the gas are aspirated through 50 c.c. of decinormal iodine solution contained in a ten-bulb tube (as shown on p. 146, Fig. 72), followed by a similar tube, filled with 50 c.c. of decinormal sodium thiosulphate solution. When the operation is finished, the contents of the two tubes are emptied into a beaker and titrated with decinormal iodine solution and starch; the number of c.c. required ($=n$) multiplied by 0·001603 gives the total sulphur present as SO_2 and H_2S. The blue coloration is then removed by addition of a drop of thiosulphate solution, methyl orange is added, and the solution titrated with decinormal sodium hydroxide solution. If the number of the cubic centimetres of this, necessary to neutralise the solution, be called m, then $(m-n) \times 0{\cdot}001603$ gives the quantity of sulphur present as SO_2.

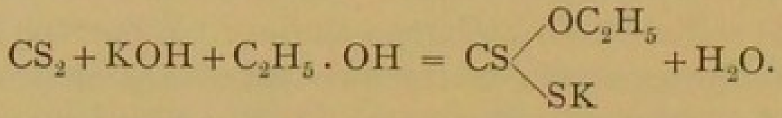
OTHER VOLATILE SULPHUR COMPOUNDS.

In coal-gas, after having passed through the oxide of iron purifiers, there are still small quantities of volatile sulphur compounds (apart from any traces of unabsorbed hydrogen sulphide). Most of this is *carbon disulphide*, the amount of which varies from 10 to 80 grains per 100 cb. ft. of gas, according to the variety of coal carbonised, and the conditions of distillation. In addition, from 5 to 10 grains of sulphur is present in the form of organic compounds, of which *thiophene*, *carbonyl sulphide*, and *alkyl mercaptans* have been detected.

The *qualitative detection* of organic sulphuretted compounds, according to Ilosvay de Ilosva (*Bull. Soc. Chim.*, 1890, p. 714), can be effected by means of a Bunsen flame, caused to strike back into the burner, at the low temperature of which (355° to 360°) the sulphur is transformed into hydrogen sulphide. In such a burner, paper soaked with lead acetate is coloured brown already within one minute, whilst in the unchanged gas such coloration (caused by H_2S) is not perceived at all, or only after much longer time).

Pfeiffer has also observed the formation of H_2S from such compounds when passing street-gas through a heated palladium asbestos tube (p. 165).

The detection of *carbon disulphide*, according to Vogel (*Annalen*, 1853, p. 369), easily takes place by passing the gas, after drying by calcium chloride, through a solution of potassium hydroxide in absolute alcohol, which causes the formation of potassium ethyl-xanthogenate (xanthate):



$$CS_2 + KOH + C_2H_5 . OH = CS\begin{cases} OC_2H_5 \\ SK \end{cases} + H_2O.$$

This is proved by distilling off the alcohol, slightly acidulating with acetic acid, and adding a solution of cupric sulphate, which produces a yellow precipitate of cupric xanthogenate.

Quantitative Estimation of Carbon Disulphide Vapour in Gases.—The methods proposed by Biehringer (*Dingl. polyt. J.*, cclxxvi. p. 28), Schmitz-Dumont (*Chem. Zeit.*, 1897, pp. 487 and 510), Goldberg (*Z. angew. Chem.*, 1899, p. 75), and Eiloart (*Chem. News*, lii. p. 184) do not seem to have found much application.

The conversion of CS_2 into xanthate just mentioned as a qualitative reaction may be utilised for a quantitative estimation by ascertaining the quantity of xanthate or of sulphur in the solution. This can be done by one of the following methods:—

(*a*) Acidifying with acetic acid and precipitating by a decinormal solution of cupric acetate in acetic acid; the xanthate precipitated has a constant composition, the ratio $CuO : CuS_2$ being 1·925. The precipitate is filtered off and the excess of copper in the filtrate determined by addition of potassium iodide and titration with decinormal sodium thiosulphate.

(*b*) Gravimetrically by boiling the alkaline xanthate solution with pure hydrogen peroxide solution, whereby the xanthate is oxidised to sulphate, which is determined by barium chloride.

Another method of estimating the CS_2 has been indicated by A. W. Hofmann (*Ber.*, xiii. p. 1732). A solution of triethylphosphene in ether is poured on caustic soda solution, contained in three wash-bottles, through which the gas is passed for several hours, and measured in the end by a meter. In presence of CS_2 the liquid in the first bottle soon shows a pink colour, and soon after crystals of an addition product of triethylphosphene and carbon disulphide are formed. When the contents of the third bottle begin to turn pink, the test is stopped. The crystals formed are collected on a tared filter, and dried *in vacuo*. One g. of the compound $(C_2H_5)_3$ PCS_2 indicates 0·392 g. CS_2.

The carbon disulphide may also be estimated by converting it by platinised pumice into hydrogen sulphide, and estimating this colorimetrically by Harcourt's method, described *suprà*, p. 251. To carry out the test, the apparatus shown in Fig. 107 is employed. A small fractionating-flask of 30 c.c. capacity, filled with platinised pumice, is placed in a special stand, surrounded by a glass chimney, so that the bottom of the flask is about 1 in. above the small ring burner fixed at the bottom of the chimney. The burner is lighted, turned down till the flame just shows a slight luminosity, and the gas thus allowed to pass, at the rate of ½ cb. ft. per hour, through the platinised pumice, which is thus heated to about 300° to 350° C. After about ten minutes the delivery tube is connected to the tube containing the lead acetate syrup, and the latter to an aspirator, and the gas passed in a thin stream through the tube until this has reached the same depth of colour as that of the standard cylinder, corresponding to

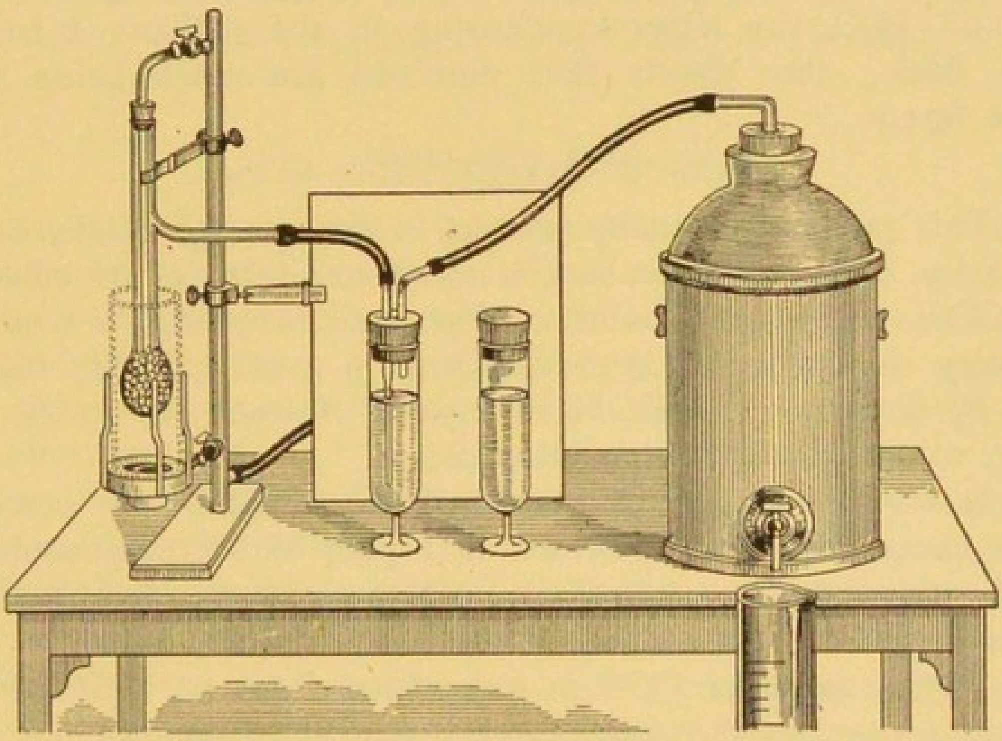


FIG. 107.

0·0025 grain or 0·000162 g. of sulphur. The volume of gas containing this quantity of sulphur in the shape of carbon disulphide is obtained from the amount of water run from the aspirator and collected in the measuring cylinder; from these data the amount of sulphur present in the gas as carbon disulphide is readily calculated. This method, whilst very rapid and convenient, only gives results of fair accuracy, if the gas tested is free from oxygen, or only contains very little of it. Mostly, however, purified coal-gas contains appreciable quantities of oxygen, which, in presence of the hot pumice acts on the H_2S produced, converting it into S and H_2O, the latter condensing in the delivery tube of the flask; the results thus obtained are much below the true figure.

CARBON OXYSULPHIDE, COS.

This gas is occasionally present in coal-gas (*J. Gasbeleucht.*, 1909, p. 288). Water absorbs about one-third of its volume of COS. An aqueous solution of potassium hydroxide absorbs it very slowly, but it is rapidly and in great quantity taken up by a solution of KOH in 2 parts of water, to which its own volume of alcohol has been added.

It can be separated from carbon disulphide by passing the gases through a mixture of 1 part of triethylphosphine and 9 parts of chloroform, which absorbs the carbon disulphide.

The presence of COS in gas mixture can be detected by passing the gas through a starch solution, coloured blue by a trace of iodine. In the presence of COS the blue tint changes first to violet, then to red, and finally the colour is entirely discharged. Of course no other gases must be present which act upon the iodide of starch.

It is indirectly detected and estimated according to York Schwartz (*Chem. Zeit.*, 1888, p. 1018), by first estimating the H_2S by passing a considerable quantity of the gas through titrated iodine solution, and then adding caustic soda solution, whereby the following reaction is produced:—

$$COS + 2KOH = H_2S + K_2CO_3.$$

After a few minutes the liquid is acidified, and the H_2S newly formed from the COS is estimated by iodine solution.

Hempel (*Z. angew. Chem.*, 1901, p. 865) determines the carbon oxysulphide in the presence of hydrogen sulphide and carbon dioxide by first absorbing the H_2S with an acid solution of cupric sulphate, then decomposing the COS into CO and S by passing the residual gases through a hot platinum capillary tube, determining the CO set free by absorption in a hydrochloric acid solution of cuprous chloride, and finally determining the CO_2 by means of KOH.

Witzek (*J. Gasbeleucht.*, 1903, p. 145) prefers the method indicated by York Schwartz (as above), which he quotes from my *Chemisch-technische Untersuchungsmethoden*, 4th ed. vol. ii. p. 614, and erroneously designates as "Lunge's method."

Total Sulphur.

In most cases, the separate determination of carbon disulphide, etc., in coal-gas is not carried out, as all the information usually required is obtained by the estimation of the total sulphur present, by burning a known volume of gas and estimating the sulphur in the products of combustion.

In Great Britain the method almost always employed is that used by the Metropolitan Gas Referees for testing London gas; it is generally known as the "Referees' Method." The gas is burnt in a small Bunsen burner, Fig. 108, which is mounted on a short cylindrical stand, perforated with holes for the admission of air, and having on its upper surface, which is also perforated, a deep circular channel to receive the wide end of the trumpet tube. On the top of the stand are placed lumps of fresh commercial sesquicarbonate of ammonia, weighing in all about 60 g. The upper, narrow horizontal end of the trumpet tube is connected by flexible tubing with the side tubulure of a vertical glass cylinder, constructed above the tubulure to about half its diameter, the space from the contracted neck to the top being filled with glass balls about 15 mm. in diameter, to break up the current of gas and promote condensation. To the top of the condenser a long glass tube, slightly bent over at the upper end, is affixed by means of a cork or rubber tubing; this serves to effect further condensation, as well as to regulate the draught and to afford an exit for the waste gases. At the bottom of the condenser is fixed a small glass tube drawn out to a jet, through which the liquid formed during a test drops into a flask beneath. The test should be carried out in a room in which no other gas is burnt, and the air of which is not otherwise contaminated with sulphur dioxide.

The gas is burned at the rate of 0·5 to 0·7 cb. ft. per hour, the trumpet tube being placed on the burner when the meter index passes a point which is noted. The products of combustion, together with the ammonia evaporated from the carbonate, pass through the condenser, where the sulphur dioxide is condensed from the products as a solution of ammonium sulphate, the excess of oxygen present effecting the oxidation of the sulphite to sulphate. As soon as the required quantity of gas has been passed, the supply is shut off. For official purposes, meters are used which are arranged to cut off the gas supply automatically when 10 cb. ft. have passed, and to record the time at which this takes place. For unofficial tests this is, of course, unnecessary. After cooling, the condenser tube and cylinder are washed out with distilled water into the beaker or flask containing the condensed liquid, and the sulphur in the latter determined in the usual way, either in the whole or in an aliquot part of the solution, by precipitation with barium chloride. From the weight of barium sulphate ob-

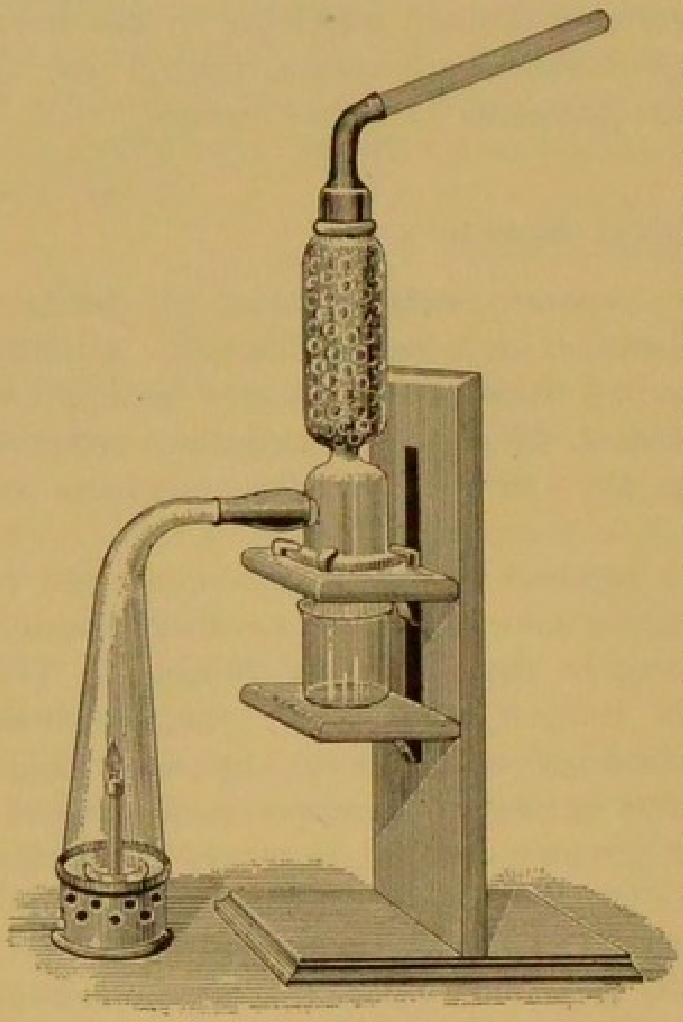


FIG. 108.

tained, in grammes, the sulphur in grains per 100 cb. ft. is readily obtained:—

$$\text{Grains per 100 cb. ft.} = \frac{\text{g. BaSO}_4 \times 15.432 \times 0.1374 \times 100}{\text{gas consumed corrected to } 60^\circ \text{ F. and 30 in. Bar.}}$$

The correction of the gas volume to 60° F. and 30 in. pressure is effected by the table in Lunge-Keane's *Technical Methods* vol. ii. pp. 690 to 691.

This method tends to give results which are slightly low owing to incomplete oxidation of the sulphites to sulphates, the former not being precipitated by barium salts. To avoid this possibility, some analysts prefer to oxidise the solution with bromine water before precipitation, whilst others oxidise with nitric acid, and precipitate with barium nitrate instead of chloride. J. Fairley (*J. Soc. Chem. Ind.*, 1887, p. 283) dispenses with the use of ammonium carbonate, and allows a solution of hydrogen peroxide to drip down the condensing cylinder of the Referees' apparatus, the sulphur being then obtained in the condensate as free sulphuric acid. Instead of using the gravimetric method, the amount of sulphuric acid may be then determined by titration with normal alkali, provided that the hydrogen peroxide solution used is neutral. Or, by using a known volume of hydrogen peroxide solution of determined acidity, the sulphuric acid formed may be found by deducting the amount of the latter from the total quantity of acid found.

H. Blair (*J. Soc. Chem. Ind.*, 1911, p. 397) has proposed the following volumetric method for the estimation of the sulphuric acid obtained by the Referees' process. An aliquot portion of the solution is boiled to volatilise the ammonium carbonate, thus leaving neutral ammonium sulphate; an excess of neutral formaldehyde solution (about 30 per cent.) is then added to the hot solution, which combines with the ammonia, forming hexamethylene tetramine, and liberates sulphuric acid, in accordance with the equation:

$$2(NH_4)_2SO_4 + 6CH_2O = N_4(CH_2)_6 + 2H_2SO_4 + 6H_2O.$$

The liberated sulphuric acid is then determined by titration with decinormal alkali, using phenolphthalein as indicator; 1 c.c. $N/10$ alkali $= 0{\cdot}0247$ g. S.

F. Fischer used for this determination the following apparatus, shown in Fig. 109, in one-tenth actual size. The gas supply, after passing the experimental meter, is burnt in the small Bunsen burner B, at the bottom of the adapter C; the latter is fitted into the bulb *n*, at *v*, either by a cork or by an asbestos ring. The tube is surrounded by a condenser K, the water supply of which enters at *a* and leaves at *w*. The water formed in the combustion condenses in the tube *n*, *n*, and there absorbs the sulphurous and sulphuric acids, the liquid products being finally collected in F. The sulphur content is determined by titration with decinormal alkali, after first oxidising the sulphurous acid with potassium permanganate; or a test-tube, containing liquor ammoniæ may be placed by the side of the burner during the combustion, in order to ensure a more complete condensation of the SO_2, and the sulphuric acid tested gravimetrically. The current of gas is regulated so that there is an excess of 4·6 per cent. of free oxygen, as can be determined by taking a sample of the exit gases at *o*; with good condensation, about 50 c.c. of liquid are collected per 50 litres of gas burnt.

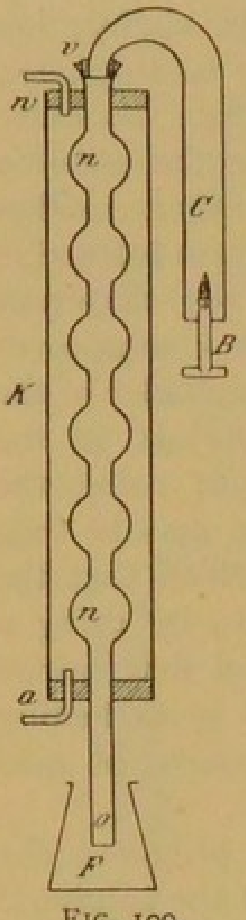


FIG. 109.

In Germany the method mostly used for the determination of total sulphur in gas is that of Drehschmidt, described in Post's *Chemisch-technische Analyse*, 1888, which we render here according to the description by Pfeiffer in Lunge-Berl's *Chemisch-technische Untersuchungsmethoden*, vol. iii. p. 294. This process, similar to those previously described by Evans and Poleck, is founded on the oxidation of the combustion products by brominated potassium carbonate solution, and has been found in prolonged use as the best in existence.

Fig. 110 shows the apparatus used for this process. The gas is first passed through an experimental gas-meter, and then to the Bunsen burner fixed gas-tight in the case A. The burner is closed with a cap of wire gauze, to prevent the flame from striking back; for the purpose of regulating the air supply it is fitted with a movable casing, adjusted in such manner that the flame is just rendered non-luminous. Case A consists of two parts, fitting into each other, one placed over the other, with a tight, conical joint. Into the lower part enter the ends of a forked tube *b* for admitting the air required for combustion.

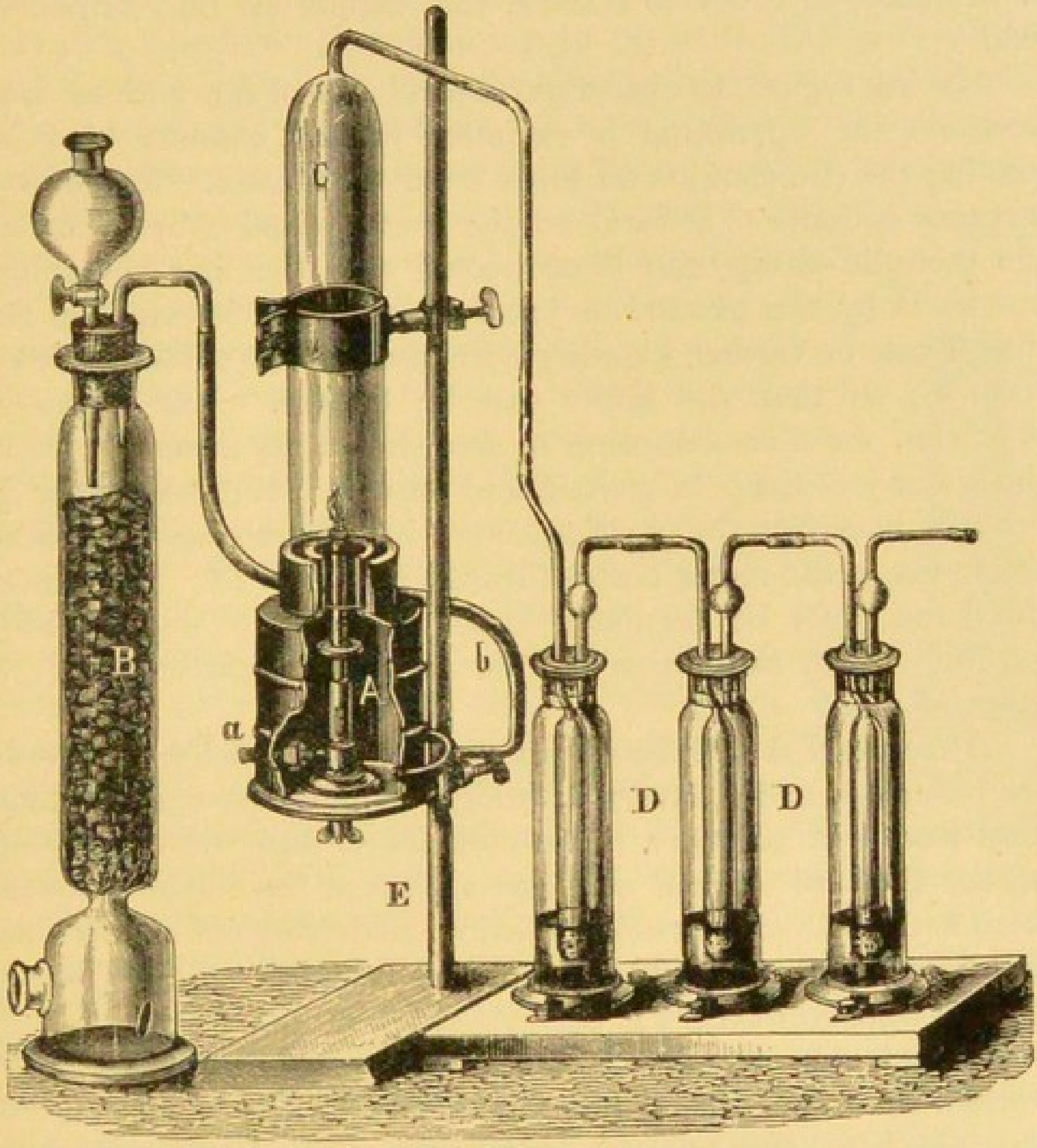


FIG. 110.

This air enters from below into the tower B, filled with bits of pumice, where it is purified from any sulphur compounds contained in it by caustic potash solution dropping down from the funnel tube at the top, and is then carried by the rubber tube *b* to the burner. The upper part of A, through which the burner passes, carries a circular pocket, filled with mercury, forming a gas-tight joint with the glass cylinder C. From this a glass tube, fused to C, carries the gases to the first of the absorption bottles DD, into which it enters by a ground-in stopper. The last of these bottles is connected with a water-jet pump. Each of the cylinders is charged with a 5 per cent. potassium carbonate solution; the first two cylinders, moreover, receive a few drops of bromine, in order to oxidise the sulphurous into sulphuric acid.

Having regard to the slight movability of the various connections, the apparatus is mounted in such manner that in making the connections no force need be applied. In the first instance cylinder C is fixed on the metal stand E by means of the metallic clamp, and is connected with the first absorbing bottle D by the ground-in joint. Case A is lowered so far that it can be turned, together with the burner, sideways away from C, so that the flame can be lighted. The flame is regulated for a consumption of from 20 to 30 litres per hour, the water-jet pump is started, and case A with the burner is brought back into the position shown in the drawing, as soon as the index of the meter passes through the point D. Sometimes the flame must be regulated again; it ought to show a sharp outline. Each estimation of the sulphur requires about 50 litres of gas.

After the test is finished, the various parts of the apparatus are taken out in the inverted order, compared to that in which they were put together. The cylinder C and the absorption bottles DD are washed out into a beaker, the liquid is acidulated with hydrochloric acid, boiled up to driving out all bromine, and dilute hot barium chloride solution is added. One g. $BaSO_4$ formed indicates 0·1373 g. S.

Contrary to Hempel (*Gasanal. Methoden*, 3rd ed., p. 256) Pfeiffer maintains that Drehschmidt's apparatus is nothing like so easily breakable as it would appear. But, after comparative trials, he employs only the principal parts of it, viz., the case A with the burner and cylinder C. These are placed on a table, the cylinder C being loosely held by an ordinary stand, and connected with the wash-bottle shown in Fig. 111 (without the elbow pipe shown there), in such manner that its delivery pipe passes through the wide entrance tube of the bottle, the joint being made gas-tight by means of a piece of rubber tubing. Through the second bore in the stopper of the wash-bottle passes the narrowed end of a calcium chloride tube, holding about 100 c.c., and half filled with bits of glass. This simple absorbing contrivance is charged with a little water and 25 c.c. of decinormal caustic soda solution, poured in through the calcium chloride tube, so that the bits of glass are equally moistened with it. Then 1 c.c. of pure hydrogen peroxide (Merck's "perhydrol," containing 30 per cent. H_2O_2) is added, and the free end of the calcium chloride tube is connected with a tube leading to the water-jet aspirator. Pfeiffer also employs a different arrangement for washing the air serving for combustion, viz., a 1-litre Woulff's bottle with two necks, through one of which passes a tube with its bottom cut off in a slanting way, just dipping into the strong caustic soda solution contained in the bottle; through the other neck passes a wide absorption-tube, holding about 200 c.c., and loosely filled with wood-cellulose. Before the test the Woulff's bottle is inclined in such a way that, by blowing through a rubber tube into the free end of the dipping-in tube, the caustic liquor is driven up in the absorption-tube and moistens the wood-cellulose. Then the free end of this tube is connected with the air-conduit *b* of Drehschmidt's apparatus. Apart from this the test is carried out as described, but it is preferable to place the wash-bottle in a tin pot filled with water, in order to prevent a too early decomposition of the hydrogen peroxide.

FIG. 111.

After finishing the passage of the gas, the absorbing liquid is washed from the calcium chloride tube back into the wash-bottle, adding in the end a drop of dimethylamidoazobenzol (methyl orange) as indicator, and the excess of caustic alkali is retitrated with decinormal acid. Each cubic centimetre of *N*/10 alkali used is equivalent to 0·001603 g. or 0·02478 grain of sulphur, and the number of grains of sulphur per 100 cb. ft. is obtained by the equation:—

$$\text{Grains per 100 cb. ft.} = \frac{\text{Number of cubic centimetres of } N/10 \text{ NaOH} \times 0{\cdot}02478 \times 100}{\text{Gas consumed corrected to 10 N.T.P.}}.$$

The exactness of this volumetrical method is proved by the fact that in the combustion no notable quantity of nitric acid is formed, that no more sulphuric acid is absorbed in a second receiver, and that the results of titration exactly coincide with the gravimetrical estimation.

The apparatus of Somerville (*J. Gas Lighting*, 1910, p. 29) resembles that of Drehschmidt. The gas is burnt at the rate of about $\frac{1}{2}$ cb. ft. per hour, and the products of combustion are aspirated through a wash-bottle containing 100 c.c. of $N/1000$ iodine solution and a few cubic centimetres of starch solution. The gas is passed through till the solution is just decolorised, when the gas meter is at once by-passed. The iodine solution employed contains 0·1268 g. I, equivalent to 0·0016 g. or 0·024688 grains of sulphur, which is, therefore, the amount present in the volume of gas burned.

Various other methods have been described for this purpose, of which we mention those following :—

Dickert (*J. Gasbeleucht.*, 1911, p. 182) employs an alkaline solution of "perhydrol" (hydrogen peroxide), which oxidises the sulphur compounds in the cold to sulphuric acid, to be determined as barium sulphate. Bosshard and Horst (*ibid.*, 1912, p. 1093) declare this method to be quite inaccurate.

Niemeyer (*J. Gasbeleucht.*, 1911, p. 1078; *Chem. Zentralb.*, 1912, ii. p. 375) estimates the sulphur dioxide iodometrically in the combustion products of the gas, and adds 6 to 8 per cent. to the value of sulphur thus found, to allow for the other sulphur compounds in coal-gas [that is surely too "rough and ready"!].

McBride and Weaver (*J. Ind. and Eng. Chem.*, 1913, p. 474) made a comparison of the Gas Referees' apparatus (*suprà*, p. 257) with the modifications proposed by Hinman-Jenkins and by Elliott, with the result that any of these apparatus is capable of giving satisfactory results if properly worked.

The same authors (*ibid.*, p. 598, and *J. Gas Lighting*, 1913, pp. 531 and 598) compare the gravimetric, volumetric, and turbidimetric methods for determining the sulphate present in solutions obtained in the Gas Referees' apparatus. For accurate work they prefer the gravimetric methods (precipitation with barium chloride). For rapid work the "turbidimeter" can be employed. This is a portable apparatus consisting of a glass cylinder, graduated in cubic centimetres, held in place above a 16 candle-power carbon filament lamp. The solution from the sulphur apparatus is neutralised with hydrochloric acid, and an additional 2 c.c. of acid (1 : 1) is added. The volume is measured, and 90 c.c. taken for the test; 10 c.c. of 10 per cent. barium chloride solution are added to the solution, which should be at 25° to 30° C., and the whole stirred for one minute. The suspension is poured gradually into the turbidimeter until the filament of the lamp cannot be seen; it is then poured back, and the turbidity again tested until the point is fixed within 1 mm. The amount of sulphur is then ascertained from tables of curves obtained previously.

This method, according to the authors, is accurate to within 2 or 3 per cent. of the quantity of sulphur present. But a critic in the *J. Gasbeleucht.*, 1913, p. 919, justly remarks that that method is necessarily inaccurate, and has no advantage over the direct titration of the acids formed in burning the gas and absorbed by a neutralised hydrogen peroxide solution.

HYDROGEN.

As a *qualitative proof* for the presence of hydrogen Phillips (*Amer. Chem. J.*, 1894, p. 259) employs dry palladious chloride, which with hydrogen forms hydrogen chloride, to be proved by the precipitation of silver chloride when afterwards passing the gases through a solution of silver nitrate. This reagent is not applicable in the presence of olefins and of carbon monoxide, which equally act on palladium chloride.

Zenghelis (*Z. anal. Chem.*, 1910, p. 729), to prove the presence of hydrogen in presence of methane, ethylene, acetylene, etc., passes the gas mixture through a solution of sodium hydroxide and then through a tube containing platinum foil or wire gauze, previously ignited, and immersed in a few cubic centimetres of a warm solution of sodium molybdate (1 g. MoO_3 dissolved in caustic soda solution and diluted to 200 c.c.). The hydrogen is occluded by the platinum and immediately reduces the molybdate, imparting to it an intense blue colour. If the amount of hydrogen is small or the test solution is old, the colour is a light greenish blue. Palladium acts even more delicately than platinum. Arsine, phosphine, and carbon monoxide must be removed before applying the test.

Pereira (*J. Amer. Chem. Soc. Abstr.*, 1913, p. 3284) detects hydrogen by means of its reducing action (production of a blue coloration) on solutions of phosphomolybdic and sodium tungstate in the presence of palladium chloride as a catalyst.

The physical method, worked out by Haber and Löwe by the help of their "interferometer" (*Z. angew. Chem.*, 1910, p. 1393; *vide suprà*, p. 177) can be also used in this case.

Quantitative Estimation of Hydrogen.—Hydrogen is practically always determined by combustion with oxygen, either by means of explosion or by the catalytic action of heated palladium or platinum. We have frequently had occasion to describe this operation in former chapters, *e.g.* pp. 71, 90, 97, 109, 129, 152, 156, 160, 162, 167, 174, where also the (generally occurring) cases are treated in which other combustible gases are present at the same time.

The determination of hydrogen by absorption in palladium hydrosol has been described *suprà*, p. 131.

Holm and Kutzbach (*Z. für chem. Apparatenkunde*, 1905, p. 130) describe an apparatus for estimating hydrogen by its strong *conductivity for heat*, principally intended for a continuous estimation of that gas in water-gas, coal-gas, or producer-gas. It does not appear to have found much practical application.

Schultze and Koepsel (*Braunkohle*, 1913, p. 740; *Z. angew. Chem.*, 1913, *Ref.*, p. 466) describe a method for the uninterrupted estimation of hydrogen in producer-gas, founded on passing the gas over electrically heated wire and measuring the difference of conductivity.

The estimation of hydrogen in the presence of *methane* will be described later on, when treating of methane.

The apparatus of Dosch, mentioned *suprà*, p. 230, may be utilised for the continuous estimation of hydrogen in producer-gases.

METHANE.

Methane (marsh-gas) cannot be estimated by absorption methods, as there are no suitable absorbents for it. It is always estimated by combustion; in the presence of hydrogen "fractional combustion" (pp. 71, 164, and 169) can be applied, as methane is not as easily combustible as hydrogen, and remains unchanged at temperatures at which hydrogen as well as other hydrocarbons are burnt. When only hydrogen has to be taken into account (*e.g.* where there are no heavy hydrocarbons present, or when these have been removed by absorbents), both hydrogen and methane can be burnt together, and the proportion of methane ascertained by estimating that of the carbon dioxide formed, whose volume is equal to that of the methane burned; the volume of oxygen required is twice that of the methane:

$$\underset{\text{2 vols.}}{CH_4} + \underset{\text{4 vols.}}{2O_2} = \underset{\text{2 vols.}}{CO_2} + \underset{\text{0 vol.}}{2H_2O}.$$

Methane is the principal dangerous constituent of the air of coal-pits, when rendered explosive by the presence of "fire-damp" ("grisou" in French). Hence Coquillion, when describing his apparatus for examining the air of coal-pits, called it "*Grisoumeter*," and this name has also been given to various other apparatus proposed for the same purpose. The principle of Coquillion's apparatus (*Comptes rend.*, 1877, clxxxiv. p. 458) is the burning of a mixture of methane and air, without explosion, by contact with heated platinum or palladium, and noting the contraction produced.

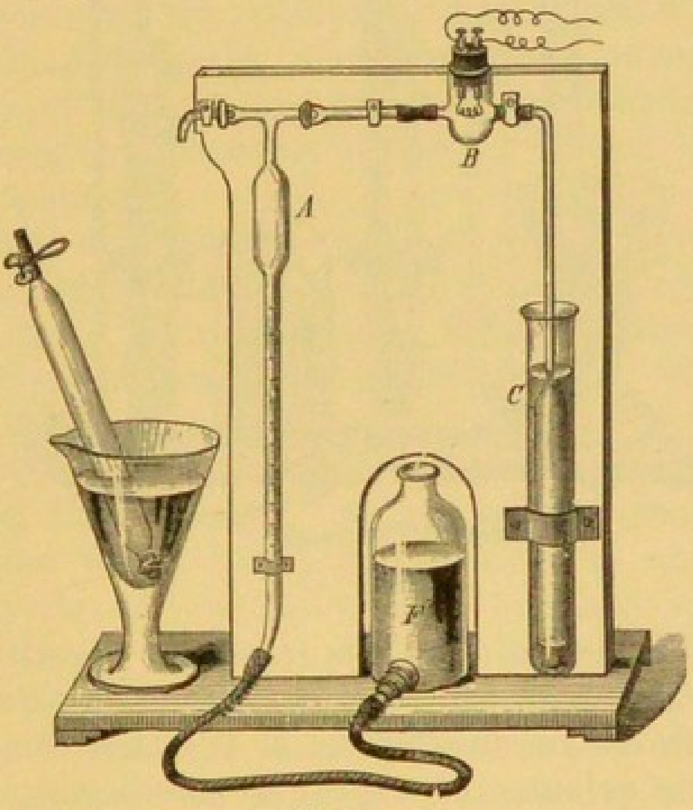


FIG. 112.

Coquillion's grisoumeter is shown in Fig. 112. A is a measuring-tube, ending at the top in a T-piece with a glass tap on each side. The tube contains from these taps down to the zero mark near the bottom, 25 c.c., but the upper, wider part is not divided, the lower, narrower part being divided in tenths of a cubic centimetre. The bottom of this tube is connected by a rubber pipe with the levelling-bottle F, by means of which A is filled and emptied, like Orsat's apparatus (p. 66). By means of the two top taps, burette A can be connected either with the reservoir containing the gas to be tested, or with the combustion-vessel B, which is hydraulically sealed by the cylinder C′. If, after combustion, the carbon dioxide formed is to be removed from the gas and measured, the apparatus is provided with an absorbing-vessel D (Fig. 113) containing caustic potash solution; this shape was called by Coquillion "Carburomètre." Here, between the gas-burette A and the combustion-vessel B, is interposed a glass vessel D, containing caustic potash solution. The vessel B is closed by a rubber cork, through which pass two brass pins, provided on the outside with screw clamps for receiving the wires from an electric battery, and connected inside B by a spiral of thin

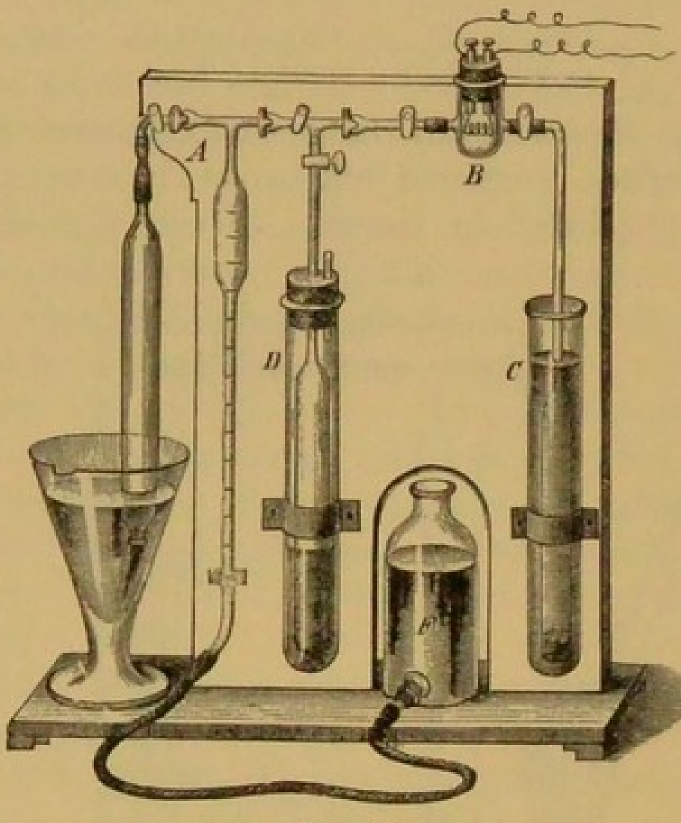


FIG. 113.

platinum or palladium wire which becomes red hot when an electric current is passed through.

This apparatus is manipulated as follows:—A is filled with water by raising F; connection is made with the outside cylinder containing the sample of gas; the latter is opened under water by removing its cork, and by lowering F the gas is transferred into A, where it is drawn in as far as the zero mark in the usual manner. Now the current is closed and the gas is passed over the red-hot platinum spiral in B by raising the levelling-bottle F, making it go backwards and forwards several times. After cooling, the contraction is noted, half of which corresponds to the methane. If there is too little oxygen present, more air (measured) must be admitted, and the passage over the red-hot platinum repeated.

The combustion takes place easily and rapidly, but the cooling takes a long time, and the results are only approximate. Small percentages of methane in the air cannot be estimated by this instrument.

The principle on which Coquillion's grisoumeter is founded has been applied by quite a number of chemists by means of other apparatus. We now describe the apparatus constructed by Cl. Winkler (*Z. anal. Chem.*, 1889, p. 286). He employed a Hempel's tubulated gas-pipette, as shown in Fig. 114. Into this pipette two brass electrodes are introduced, 175 mm. long, 5 mm. thick, *not* varnished. At the bottom they have holes for the current wires; at the top, incisions in which the two ends of a platinum spiral wire fixed by small screws. This spiral consists of platinum wire 0·35 mm. thick, made by coiling the wire over a steel pin 1·3 mm. thick, and leaving at the ends 1 cm. for fixing it in the above-mentioned incisions. Before doing so, the electrodes are passed through a twice-perforated cork (not shown in the drawing), which reaches half-way up and prevents them from moving. These electrodes must be 2 or 2·5 cm. distant from the top of the pipette, which is completely filled with water and kept closed in the usual manner. This apparatus is manipulated in the following manner:—The gas, previously freed from absorbable constituents and (by "fractional combustion," pp. 71, 164, 169) from hydrogen, and thus containing only methane and nitrogen, is measured in a Hempel's burette and mixed with a measured excess of air. This burette is connected by an ordinary glass capillary with the pipette, Fig. 114, and the current closed. Now the levelling-tube of the burette is lifted up with the left hand, one of the pinchcocks is opened entirely, the other one partly with the right hand, and thus the gas is *slowly* transferred into the pipette. As soon as the water-level has sunk below the platinum spiral, this becomes red hot. Now the entrance of the gas must be interrupted for a moment and the remainder of the gas introduced very gradually, by which proceeding the combustion is made to take place quietly and without any risk of an explosion. If, however, the gas is passed in too quickly, or if it is first introduced into the pipette and the current is then closed, an explosion may take place which throws out the stopper containing the electrodes, and the water out of the side-bulb. The thickness of the wire and the number of coils must correspond to the strength of the current. The above-mentioned dimensions refer to a current from two small Grove elements. If the wire is too thin, it fuses; if it is too thick, it does not get hot enough, but it is not difficult to hit the proper proportions. The combustion is finished within one minute. Now the current is shut off, the pipette (the upper part of which gets rather hot) is allowed to cool down, the gas is retransferred into the burette, the carbon dioxide is removed by means of a caustic potash pipette, and the total contraction noted. By dividing the latter by 3 the volume of the methane is found.

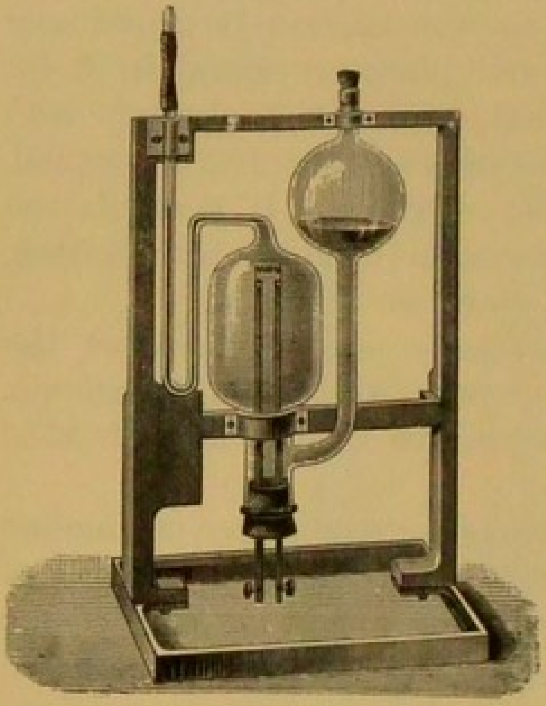


FIG. 114.

Dennis and Hopkins (*Z. anorg. Chem.*, 1899, xix. p. 179) modify Winkler's apparatus by filling the pipette with mercury and slightly modifying the electrodes.

Winkler's process can be applied to the estimation of methane in natural heating gas, in "blowers" of coal-pits, in marsh-gas, producer-gas, etc. First remove by absorption successively, carbon dioxide, heavy hydrocarbons, oxygen, and carbon monoxide, by the methods indicated *suprà* in several places (*e.g.*, p. 64 and 152), then hydrogen by combustion with air and palladium asbestos (p. 164), and now burn the methane as just described.

Leonard A. Levy (*J. Soc. Chem. Ind.*, 1912, p. 1153) describes a new apparatus for the examination of the air of coal-pits, for estimating methane, carbon dioxide, and oxygen. The methane is burned in a silicon capillary (0·5 to 1 mm. inside diameter) of appropriate form, in which a platinum wire can be heated to a white heat by the electric current. Owing to the narrow inside space, the gas is prevented from passing too quickly through it, and complete combustion is assured. The apparatus is made in two modifications, one of which serves only for a rapid estimation of methane, the other for methane, CO_2, and O. Both are sold by Alexander Wright & Co., Ltd., Westminster.

Other "Grisoumeters" have been constructed by a number of chemists as follows:—

Mertens (*Z. anal. Chem.*, 1887, p. 42).
Thörner (*Z. angew. Chem.*, 1889, p. 642).
Jeller (*Z. angew. Chem.*, 1896, p. 692).
Burell (*J. Ind. Eng. Chem.*, iv. p. 96).
Wendriner (*ibid.*, 1902, p. 1062).
Rosen (Ger. P. 245367).
Akkumulatorenfabrik, Berlin (Ger. Ps. 268736, 268737, 268844, 268845, 269131).
Kraushaar (Ger. P. 268898).
Beckmann (Ger. P. 268963).

The combustion of methane by explosion has been described *suprà*, pp. 156 and 171.

A special treatise on the analysis of coal-pit gases has been written by O. Brunck (*Chemische Untersuchung der Grubenwetter*, Freiberg, 1900).

A qualitative reaction on methane, according to Hauser and Herzfeld (*Ber.*, 1912, p. 3515), is afforded by the action of ozonised oxygen, whereby formaldehyde is formed, which is recognised by its smell, or by the action of morphine-sulphuric acid (Mannich, *Arb. Pharmaz. Inst.*, Berlin, 1906, p. 227).

Hauser (*Anal. fis. quim.*, 1913, p. 280; *Chem. Soc. Abstr.*, 1913, p. 720) points out that in the analysis of combustible gases by explosion an appreciable error is caused by the combustion of nitrogen, but the presence of 8·33 per cent. of methane ensures that the combustion of N is inappreciable.

Cl. Winkler's Method of Examining Coal-pit Air containing Very Small Quantities of Methane.—It is frequently assumed that the prevention of danger from fire-damp in coal-pits need only extend to ascertaining whether the atmosphere of the pit contains enough methane to make it inflammable or explosive, various apparatus for which has been described above. This is, however, a mistake. The mining engineer must try to prevent any accumulation of fire-damp *before* the percentage of methane has reached the lower limit of explosiveness. By the examination for methane, both in the branch current and in the principal current of air issuing from the pit, he must carefully establish the average composition of the pit-air, as it changes with the progress of working the coal-seams. In all such cases it is necessary to determine comparatively small quantities of methane, such as cannot possibly be read off in a gas-burette with any degree of exactness. The following process, however, attains the desired end in a simple manner. It consists in burning the methane contained in a large volume of pit-air by means of electrically glowing platinum, and then estimating the carbon dioxide formed by *titration*. This process has been thoroughly tested in the Freiberg Mining Academy, and it has been established there that a stream of induction sparks, even of considerable length, cannot replace the electrically glowing platinum.

All the operations of measuring, burning, and titrating are carried out in the conical flask A, Fig. 115, which during the combustion is turned upside down, as shown in the figure. On its neck it has a circular mark, up to which it is ordinarily closed by a twice-perforated rubber cork, with glass rod stoppers. The contents of the flask up to this mark are ascertained by weighing or measuring, and are marked on the glass by etching; it should generally hold about 2 litres, but in the case of gases containing much methane, 1 litre is enough.

When the flask has to serve for a combustion of the gas contained in it, its stopper is taken out under water and replaced by a rubber cork *k*, with electrodes *e*. A second perforation, otherwise closed by a glass rod, serves for introducing by means of a pipette a certain volume of water, say

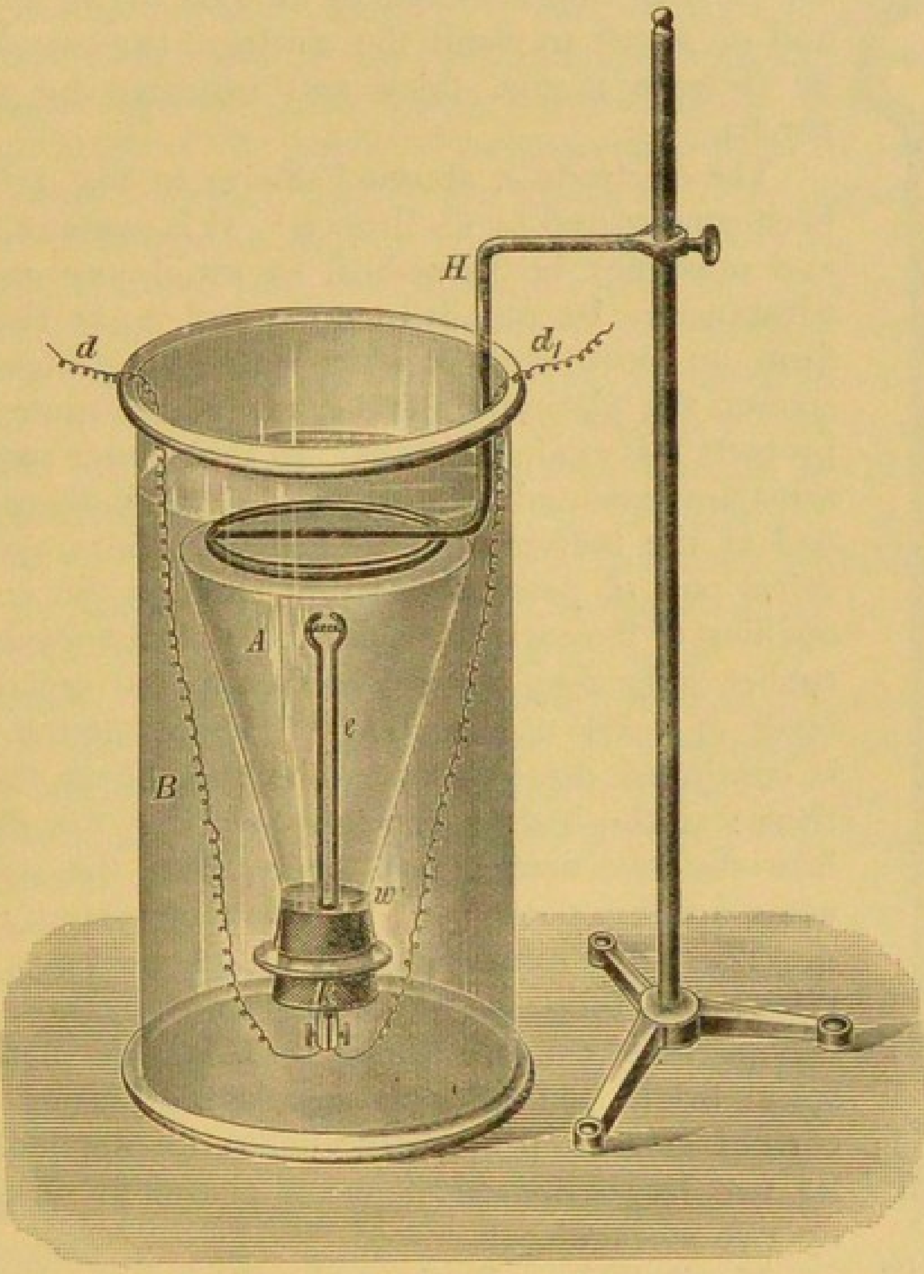


FIG. 115.

10 c.c. This water during the combustion prevents the contact of the gas with the rubber, which might produce considerable errors; when turning the flask upside down, it forms the protecting layer *w*. Its volume must be known, as well as that of the electrode *e*, and these amounts must be deducted from the contents of flask A.

Lest this flask should get hot during the combustion, it is immersed in the water-filled beaker B, and prevented from rising up by the adjustable holder H, as shown in the figure. If instead of a glass beaker, a tin vessel is employed, that holder can be fixed to its side. The wires d and d_1, which transmit the electrical current, should be at least 1 mm. thick and insulated by gutta-percha.

FIG. 116.

The electrode e, shown half-size in Fig. 116, has been constructed by O. Brunck.[1] It is made of brass and must not be varnished, to avoid any organic substances. Its parallel arms a and a_1, at the top form an open ring b, which carries, by means of screws, the platinum spiral c, and at the same time protects this against shocks. In their lower part the arms are insulated by a strong strip of india-rubber, and at the bottom they are continued into a cylindrical part d, passing gas-tight through the central opening of the cork of flask A, so that the insulating rubber strip does not project above the protecting layer of water w (Fig. 115). This insulating strip is continued downwards to the end, being thinner there; at the bottom the holes e and e_1 are drilled into the two arms; into these holes the current wires are introduced and held fast by screws f and f_1. The spiral e consists of platinum wire, 0·35 mm. thick; the total length of wire within the screw clamps is 7 cm. In order to heat this platinum spiral bright red, without any fear of fusing it, a current of 8 or 9 amperes should be applied, *e.g.*, by two large Bunsen elements placed in series, or by two storage-cells.

Manipulation.—Flask A is filled with distilled water carried into the coal-pit, and the water run out on the spot where the sample of gas is to be taken. The flask is closed by its twice perforated cork, and taken into the laboratory. If the sample had been taken in another vessel, *e.g.*, the zinc cylinder shown in Fig. 14, p. 16, flask A is filled from this in

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[1] It is sold by Louis Jentzsch, Silbermannstrasse 1, Freiberg, in Saxony.

the laboratory, taking care to let the inlet-tube end at the highest point of the flask, previously filled with water and inverted under water, so that the gas comes into the least possible contact with the water.

After filling the flask A with the gas to be examined, it is closed by the other rubber cork, provided with the electrode *e*, the exchange of corks being effected under water of the temperature of the room. The protecting-water *w* is put in, the current wires d and d_1 are attached, A is placed in the water contained in B, and fixed by the holder H. Now the current is closed and the platinum spiral kept at a bright red heat for half an hour, in order to burn the methane completely by the oxygen, which is always present in excess in such cases. Then the current is interrupted, the electrode cork is replaced by the ordinary cork, and the carbon dioxide is titrated by baryta water, as described on pp. 136, 142, and 223. As a rule, the baryta water can be run in from the burette without taking out the cork. The volume of gas employed must be reduced to normal conditions (0° or 15° and 760 mm.).

Heavy hydrocarbons and carbon monoxide should not be present in the gas. Carbon dioxide is generally present; it must be estimated in another sample of gas, *e.g.*, by the method of Hesse, p. 135, and deducted from the total CO_2 found after combustion.

Example—

Contents of absorbing bottle	2000·0 c.c.
Less—Protecting water, 10; volume of electrode, 6; baryta water added after combustion, 20 . .	36·0 „
Gas really employed for the test	1964·0 c.c.
Reduced to 15° and 760 mm.	1741·0 „
20 c.c. baryta water correspond to normal oxalic acid . .	20·6 „
Required for retitration „ „ . .	4·3 „
Difference . . „ „ . .	16·3 „
Equal to	0·93 per cent. CO_2 by vol.
Deduct CO_2 previously found in the gas by another test	0·33 „ CO_2 „
Leaving for methane	0·60 „ CH_4 „

The just-described method requires an electric current which, if it has to be specially produced, makes the apparatus rather complicated. This is avoided by the application of the Drehschmidt platinum capillary, described in a former chapter (p. 100), in connection with a Hempel pipette, or even with an Orsat apparatus.

Extremely small quantities of methane (or any other combustible gas) can be burned by hot cupric oxide. This method, fully worked out by Fresenius, has been employed by Winkler and others also for the examination of pit-air. The apparatus and method are fully described in the second English edition of Winkler's *Technical Gas-Analysis*, translated by Lunge, 1902, pp. 164 *et seq.* We abstain from doing so here, as the somewhat complicated apparatus and manipulation required make that method hardly count as a "technical" one, and it will be but rarely applied in practical cases. We have, moreover, described in a former chapter Jaeger's process for the combustion of gases by means of cupric oxide, and mentioned some other processes of this class (p. 172).

Hempel (*Z. angew. Chem.*, 1912, p. 1841) states that in a Drehschmidt platinum capillary (p. 100) the temperature at which methane is completely burned is not reached when heating by a Bunsen burner, but complete combustion is obtained by employing a capillary, made of well-fused quartz, almost entirely filled with the platinum capillary. Explosions are prevented by passing the gaseous mixture very slowly through the red-hot capillary. He employs quartz-glass tubes also for the Winkler combustion capillary (p. 165). The fractionated combustion of mixtures of hydrogen and methane by means of palladium asbestos, according to Cl. Winkler (p. 165), is best performed by means of a Bunsen burner, over which a piece of brass is fixed, on which the capillary is lying in a mercury bath. The heating is carried on up to the boiling of the mercury bath. Opinions differ as to the accuracy of this separation of hydrogen and methane by fractionated combustion, but Hempel has found it to be perfectly accurate, if care is taken that the palladium asbestos is not heated beyond 400°, which is easily done by the just-mentioned apparatus, and if the gaseous mixture is passed very slowly through the capillary. He also worked on Paal and Hartmann's method of absorbing the hydrogen by colloidal palladium (mixed with sodium picrate), avoiding the otherwise very awkward frothing by interposing between the bulb and the capillary of the absorbing-pipette a glass tube, 2 c.c. long, and 7 c.c. wide, containing a piece of platinum wire-netting. He describes a pipette specially adapted to this purpose.

Haber's "Schlagwetterpfeife" (detonating-air whistle). This is the name Professor Haber has given to the instrument invented by him for indicating the presence of a dangerous percentage of methane, etc., in pit-air, and described in *Naturwissenschaften*, 1913, p. 1049, *Chem. Zeit.*, 1913, p. 1339, and *J. Soc. Chem. Ind.*, 1914, xxxiii. p. 54. He points to the well-known fact that the Davy pit-lamp does not with certainty prevent explosions, and that all the other indicators for this purpose have drawbacks in one or the other direction. All the apparatus based on chemical reactions suffer under the drawback that methane reacts only at a red heat, and any reactions compelled at lower temperatures are not reliable for pitmen's purposes. Therefore Haber, with the co-operation of Dr Leiser, turned to physical indications. They first improved Rayleigh's "Interferometer" to such an extent that it could be regularly employed underground by experts, and allowed to judge of the methane percentages to tenths of a per cent., as described *suprà*, p. 177. It is founded on the alterations of the optical density of the atmosphere by the admixture of methane, but is not suitable for use by pitmen in actual work. Therefore Haber and Leiser turned to a method indicating the presence of methane by acoustical means, already indicated by Jahoda in the *Transactions of the Vienna Academy of Sciences in the year* 1899, which they realised by the construction of their "detonating-air whistle," shown in Fig. 117.

Within a smooth cylinder, *a*, 250 mm. long and 60 mm. diameter, the two whistles, for air and for the gas, are placed. At *b* a passage, which can be closed by a small screw, leads to the air whistle. The air passes downwards in the direction of the arrow, then turns upwards up to the small mica disc *c*, then again downwards, rises upwards in the spiral pipe *d*, and issues at *e*. If the pipe is charged in this way with pure air and closed by the small screw at *b*, the air is retained within the whistle by the action of the narrow spiral *d*, and cannot get mixed with the pit-air, whilst the spiral pipe allows it to extend. In a similar way the way of the pit-gas whistle goes first downwards from the entrance *f*, passes a filter at *g*, and a layer of soda-lime at *h*, whereby the pit-air is purified from dust, moisture, and carbon dioxide; it then goes upwards to the mica disc *t*, then downwards, and ultimately up to the valve *k*, through which it passes to *l*, where a tube, not indicated in the diagram, takes it to a point *m*, from which it passes into the space *n*. The latter forms part of an air-pump which is set into motion by drawing the cylinder *a* down. If thus a vacuum is produced at *n*, the pit-gas enters at *f* and proceeds in the above-stated way. If now the cylinder *a* is let go, it is pulled back by the vacuum, produced on pulling down over the plug *o*, connected with the cylinder; the pit-gas is forced back through pipe *m*, past the closing valve *h* to the opening valve *p*, and it passes through *r* and *q* to the mouth-pieces *s* and *t* of both whistles, which thereby are made to give sound. The air and the pit-gas in the whistle-tubes, the quality of which determines the height of the sound, are tightly shut off from the gas pressing against them by the thin mica discs *c* and *i*. Thereby it has been ascertained that the contents of the whistles, especially that of the pure air whistle, do not get mixed with the pit-gas blowing against them, unless they are emptied on purpose. In order to set the apparatus into motion, one need only pull down the cylinder *a* a little and let it go again. The sound produced thereby, which beginning from 1 per cent. methane shows distinctly countable pulsations, and in case of a dangerous percentage of methane a rapid tremulation, is audible up to 300 ft. in a straight line. A drawback of this instrument is that it does not give the signal automatically, but it must be set into motion each time, whilst the flame of the ordinary pit-lamp of its own accord rises up, certainly only in case of a high percentage of methane, or is extinguished; small percentages of

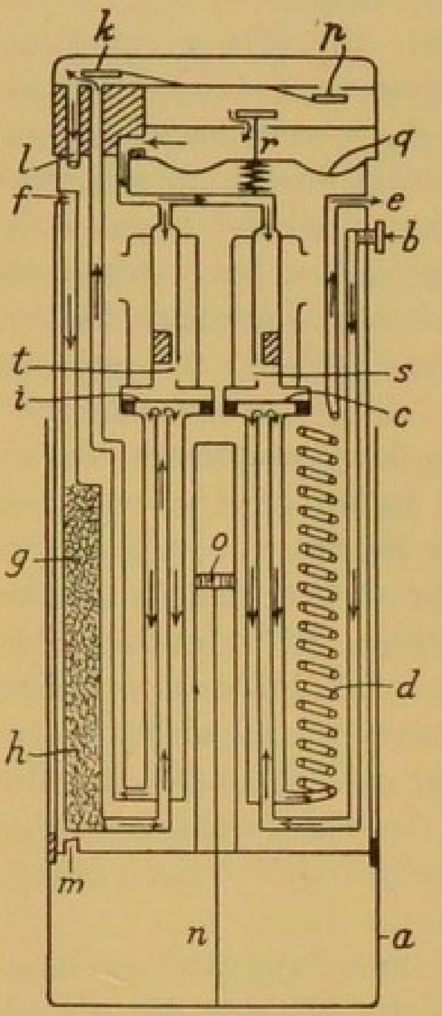

FIG. 117.

methane can be observed only by screwing down the flame, and exact observation.

Mixtures of Hydrogen with Saturated Gaseous Hydrocarbons (Methane, Ethane, Propane, etc.).

Lebeau and Damiens (*Comptes rend.*, 1913, clvi. pp. 144 and 325) cool the gaseous mixture either by liquid air, or by a mixture of solid carbon dioxide and acetone, or by petroleum ether cooled by liquid air, and subject it then to fractional distillation. Hydrogen and methane cannot be separated in this way, but this is not very material, since such a mixture can be analysed by endiometric combustion. But a mixture of hydrogen and ethane, after cooling by liquid air, can be smoothly separated by fractional distillation into its constituents. Mixtures of hydrogen, methane, and ethane, or of hydrogen, methane, and propane, can be in such a way separated into ethane or propane on the one side, and a mixture of hydrogen and methane on the other. The composition of both these mixtures can be afterwards ascertained by the eudiometric method.

In order to analyse eudiometrically a mixture of ethane, propane, and butane, it is separated into two fractions, one of which contains the ethane with a little propane, the other only isobutane with the remainder of the propane. This separation is effected by cooling the gaseous mixture below −120°. The presence of normal butane is recognised by fractionating the last portions. In such cases where the gaseous hydrocarbons are mixed with the vapours of liquid hydrocarbons, first of all by cooling down to −78°, all the gaseous hydrocarbons, together with a small portion of the vapours of the liquid hydrocarbons are separated. At −100° the pentanes do not possess any sensible vapour tension, so that the gaseous hydrocarbons can be separated from them.

This work is continued *eodem loco*, p. 557 (*vide Chem. Zentralb.*, 1913, pp. 841, 1061, 1229; and *Abstr. Amer. Chem. Soc.*, 1913, p. 1338).

Mathers and Lee (*Chem. Eng.*, 1913, p. 159; *Chem. News*, 1913, cviii. p. 80) a little later worked out an entirely similar method for the determination of hydrogen, methane and nitrogen. They point out that combustion of these gases by explosion with oxygen, the method generally used until a few years ago, in consequence of the incompleteness of the combustions gives too high a result for nitrogen. Much better is the Winkler method (*suprà*, p. 92); but there is a difficulty in fastening the platinum spiral in such a way that no other metal is exposed to the action of the hot oxygen, and if the spiral is sealed through glass, this is liable to crack. A source of error, always present when effecting the combustion over mercury, is the oxidation of the mercury if the temperature is too high, or the incompleteness of the combustion if it is too low. This error is avoided by the use of the Drehschmidt platinum capillary, but this is very expensive. Equally good results are obtained by a quartz tube, 30·5 cm. long, 7·25 mm. outside and 3·38 mm. inside diameter, filled two-thirds with platinum scrap, consisting of short lengths of wire (which in their case weighed 11·189 g.). A mercury pipette, holding the gas to be burned and the oxygen required for the combustion, was connected to one end of the quartz tube by a capillary tube with rubber connections. In a similar manner a mercury burette, with a water-jacket, was connected to the other end of the quartz tube, pinchcocks being placed on the burette and on the pipette. The heating of the quartz tube was effected by a Bunsen burner with a wing tip, producing a broad flame, an asbestos board suspended 5 mm. above the tube lessening the radiation of heat. Before starting, the temperature of the gas in the pipette was read; the pinchcock connecting the burette to the quartz tube was opened, and the burner lighted for three minutes; the increase of the volume of air being cared for in the burette. Then the pinch cock connecting the pipette to the quartz tube was opened, and the level bottle raised so that the gas and oxygen passed slowly over the hot platinum, generally three minutes being required. Then the gas, by means of the level bottle, was forced back into the pipette, and again into the burette. Now the flame and the asbestos board were removed, water was poured over the quartz tube to cool it, the pinchcock on the side of the burette was closed, and the mercury in the burette and the level-tube levelled. When the thermometer in the water-jacket showed constant temperature, the volume of gas in the burette was read and corrected for variation from the initial temperature. A correction must be made for the CO_2 which remains in the quartz tube after the combustion.

Marc Landau (*Comptes rend.*, 1912, clv. p. 403; *Chem. Zeit.*, 1912, p. 1385) shows how by the application of ultra-violet rays a mixture of *ethylene*, *ethane*, and *hydrogen* can be analysed. First the unsaturated hydrocarbon is polymerised, the ensuing contraction of volume is measured, and thereupon, after adding oxygen, the "photo-combustion" of the saturated hydrocarbons is effected. Daniel Berthelot and Gaudechon (*Comptes rend.*, clv. p. 521; *Chem. Zeit.*, 1912, p. 1472) remark that pure methane resists to the ultra-violet rays, but in the presence of oxygen hereby a far-reaching condensation takes place, hydrogen, carbon dioxide, and water being consumed, and paraffins, not attackable by sulphuric and nitric acid, being formed.

Campbell and Parker (*Trans. Chem. Soc.*, 1913, p. 1292) burn the hydrogen in such mixtures by palladium black, heated to 100°.

Czakó (*J. Gasbeleucht.*, 1914, p. 169) points out that the previously employed absorbents, especially cuprous chloride and bromine water, always take up as much methane, hydrogen, and nitrogen as corresponds to the water they contain.

ACETYLENE.

We have already mentioned this hydrocarbon in several places, *e.g.* pp. 118, 119, 132, 147.

The following *qualitative reactions* have been described for the discovery of acetylene.

Ilosvay de Nagy Ilosvay (*Ber.*, 1899, p. 2698) employs the characteristic formation of red copper acetylide $(Cu_2C_2H_2)O$ in the following way:—One g. cupric sulphate is dissolved in a 50 c.c. flask in a little water, 4 c.c. of concentrated liquor ammoniæ, and then 3 g. of hydroxylamine chloride is added; the solution is agitated until decolorised, and at once diluted up to the mark. A few cubic centimetres of it are put into a 500 c.c. stoppered cylinder, the gas to be examined for acetylene is passed over it, until the colour of the reagent changes into pink; the cylinder is then stoppered and agitated, whereupon a red precipitate is formed, if acetylene is present. Or else the gas is passed through a small bulb tube, containing glass-wool soaked with the reagent. This reagent keeps about a week if covered with petroleum, but, according to Pollak (quoted by Treadwell, ii. p. 533), much longer, up to twelve months, if copper wire is placed in it.

Llorenz (*Chem. Zeit.*, 1912, p. 702) also employs the reaction of acetylene on cuprous compounds. Makowka (*ibid.*, p. 297) points out that he had made this observation long before, and published it in detail in *Z. anal. Chem.*, 1907, p. 125.

Quantitative Estimation of Acetylene.

This may be done by combustion with oxygen, when 1 vol. C_2H_2 yields 2 vols. of CO_2; according to the reaction:

$$\underset{\text{2 vols.}}{2C_2H_2} + \underset{\text{5 vols.}}{5O_2} = \underset{\text{4 vols.}}{4CO_2} + 2H_2O.$$

But this method is only applicable in the not very frequent cases where there are no other combustible gases present.

Usually, therefore, acetylene is estimated by absorption in ammoniacal cuprous chloride solution, or in fuming sulphuric acid (*suprà*, pp. 118 and 132), or by means of its silver compounds, etc. (p. 147).

Lebeau and Damiens (*Bull. Soc. Chim.*, 1913, xiii. p. 560) estimate the acetylenic hydrocarbons by an alkaline solution of potassium iodomercurate, and the ethylenic hydrocarbons by absorption in a solution of uranyl or tungsten or molybdene sulphate in concentrated sulphuric acid.

The determination of the *yield* of acetylene from calcium carbide, which does not belong to the domain of technical gas-analysis proper, is described in detail in the paper by Lunge and Berl, in Lunge's *Technical Methods of Chemical Analysis*, translated by Keane, vol. ii. pp. 590 *et seq.* (1911).

Estimation of the Impurities contained in Crude Acetylene.

Crude acetylene, as manufactured from commercial calcium carbide, may contain the following impurities; up to 4 per cent. altogether: hydrogen sulphide, hydrogen phosphide, ammonia, carbon monoxide, hydrogen, methane (this has never been proved with certainty), nitrogen, and oxygen, but only the two first of these are seriously objectionable, as they impart an unpleasant smell to the gas, render it poisonous, and give rise to injurious acid products on combustion. Ammonia (which occurs only in traces) is also objectionable, as it aids in the formation of compounds of acetylene with metals, and is also injurious in the purification by bleaching-powder.

The estimation of *hydrogen sulphide* and *hydrogen phosphide* in crude acetylene by the process of Lunge and Cedercreutz has been described on p. 150.

Eitner and Keppeler (*J. Gasbeleucht.*, 1901, p. 548) state that in this method, where the acetylene is passed through bleaching-powder solution, certain organic phosphides are overlooked, because they are not burned to phosphoric acid by the hypochlorite (according to Keppeler, *ibid.*, 1904, p. 62, in this operation now and then explosions occur through the formation of nitrogen chloride). They prefer burning the acetylene by means of oxygen under a glass hood, as described by Drehschmidt for the estimation of sulphur in coal-gas (p. 260), and passing the gases through two ten-bulb tubes, the first of which contains water, the second a solution of sodium hypobromite (prepared from caustic soda solution and bromine), then through an empty Peligot receiver, followed by a water-jet pump, by which the current of gases is regulated in such manner that the bubbles in the ten-bulb tubes can be just counted. Much of the phosphorus pentoxide formed separates already in the glass hood, which must therefore be washed with weak hydrochloric acid, evaporating the washings with addition of ammonium bicarbonate, in order to separate any silica taken out from the glass; the filtered solution is added to that taken out of the bulb-tubes, and the phosphoric acid contained therein estimated by the molybdene method, the sulphuric acid in the filtrate therefrom as barium sulphate. They state that by this process more phosphorus is found than by the hypochlorite method. According to Keppeler (*ibid.*, 1903, p. 777) the combustion may be carried out with atmospheric air, in the place of oxygen, in which case the gases are conducted through a ten-bulb tube, the first bulbs of which contain bits of "Resistenzglas"; the SO_2 contained in the condensing water is to be oxidised by bromine.

According to Vogel (*Handbuch für Acetylen*, p. 273),

N. Caro had worked out the same method some time before, and constructed a portable apparatus for it. By the combustion methods, also the *silicon compounds* contained in the gas can be estimated, by burning the acetylene under a hood of platinum and nickel, passing the gases through pure caustic soda solution (prepared from sodium), adding bromine water, filtering off the silicic acid, and estimating the phosphoric and sulphuric acid in the filtrate.

Fränkel (*J. Gasbeleucht.*, 1908, p. 431) combines with the above method an estimation of the yield of acetylene from calcium carbide.

Lidholm (*Z. angew. Chem.*, 1904, p. 1452; *cf.* also Hinrichsen, *Chem. Zentralb.*, 1907, ii. p. 1356) describes another apparatus for this purpose.

Willgerodt (*Ber.*, 1895, p. 2107) proposed oxidising the sulphuretted and phosphoretted hydrogen by bromine water; but this method is objectionable, because bromine acts too strongly on the acetylene itself.

Mauricheau (*J. Gasbeleucht.*, 1908, p. 257) estimates the phosphoretted hydrogen in crude acetylene volumetrically. He first takes out H_2S and NH_3 by caustic potash and sulphuric acid, shakes up the remaining gas with centinormal iodine solution, and after ten minutes retitrates the excess of iodine. Each cubic centimetre of centinormal iodine solution corresponds to 0·055 c.c. PH_3 in a litre of acetylene (at 15° and 760 mm.). The relation between the iodine solution and the phosphoretted hydrogen is established by an experiment with crude acetylene of known contents of phosphorus.

Hempel and Kahl (*Z. angew. Chem.*, 1898, p. 53) measure the crude acetylene in a gas-burette filled with mercury, force it into a gas-pipe filled with mercury containing 3 c.c. of an acid solution of cupric sulphate (prepared from 15 g. crystallised cupric sulphate, 100 c.c. water, and 5 c.c. of dilute sulphuric acid, 1 to 5 c.c. water, and previously saturated with acetylene), agitate for three minutes, and measure the remaining gas, one-fourth of which indicates the PH_3. (This method contains several sources of inaccuracies.)

Other sulphur compounds (apart from H_2S) also occur in technical acetylene, as shown by Lunge and Cedercreutz, *loc. cit.* This is mentioned by Moissan and others. These sulphur compounds are oxidised in their method by the hypochlorite solution, and can be estimated, if solutions free from sulphuric acid are employed in this method.

Ammonia hardly ever occurs in sensible quantities in crude acetylene, and never in such quantities that it can be estimated by titration; this must be done by "Nesslerising."

According to the rules laid down by the German Acetylene Union (*Chem. Zeit.*, 1906, p. 607), calcium carbide is only saleable if the gas yielded by it contains at most 0·04 per cent. phosphorus compounds, calculated as hydrogen phosphide. The allowable difference of analyses is 0·01 per cent. When fixing the *hydrogen* contents in crude acetylene, all the gas must be driven out of the carbide. If the small quantities of the other impurities are to be determined, about 500 c.c. of the crude acetylene must be treated with Nordhausen sulphuric acid which absorbs acetylene and ammonia; the other gases must be determined in the gaseous remainder by the ordinary methods of analysis.

As *general reagent for injurious admixtures* in crude acetylene, Keppeler (*J. Gasbeleucht.*, 1904, p. 461) employs (as Bergé and Reychler had previously done) a solution of *mercuric chloride* containing free HCl, in which those impurities cause a precipitate. It is convenient to employ black filtering paper, soaked with mercuric chloride solution (on sale by E. Merck in Darmstadt), which before the test is moistened with 10 per cent. hydrochloric acid, and held over an open acetylene burner, without lighting the gas. In the presence of phosphorus, sulphur, and silicon compounds, a white spot appears on the paper, but not in the case of pure acetylene.

Gatehouse (*Acetylene*, 1909, p. 80) recommends white paper soaked in an ammoniacal solution of silver nitrate. With properly purified acetylene the paper will remain unchanged for at least half an hour; with impure gas it will become black in a few minutes.

Rossel and Landriset (*Z. angew. Chem.*, 1901, p. 77) analyse crude acetylene in a 100 c.c. Hempel burette filled with mercury, in which they absorb the acetylene by 30 c.c. fuming sulphuric acid; afterwards they estimate oxygen by potassium, pyrogallate, hydrogen and methane by the explosion pipette, and the oxygen by difference. [Looking at the small volumes in question, 0·1 to 0·2 c.c., this method, where the gas has to be carried backwards and forwards several times, is most uncertain.]

A complete analysis of acetylene, which will hardly ever be required for technical purposes, is described in papers by Haber and Oechelhäuser, von Knorre and Arendt, and Fränkel.

ETHYLENE.

As we have noticed in several places, ethylene can be removed and estimated by absorption by fuming sulphuric acid (p. 118) or bromine (p. 119), but this becomes more complicated when, as is mostly the case, other heavy hydrocarbons, especially benzene vapour, are present.

Berthelot (*Comptes rend.*, lxxxiii. p. 1255) proposed first removing the ethylene by bromine water, and subsequently benzene by fuming nitric acid; but this is quite incorrect, according to the unanimous judgment of Cl. Winkler (*Z. anal. Chem.*, xxviii. p. 282), Drehschmidt (in Post, *Chem.-techn. Analyse*, 2nd ed., i. pp. 108 and 109), and Treadwell and Stokes (*Ber.*, xxi. p. 31).

Drehschmidt (Muspratt-Stohmann's *Techn. Chemie*, 4th ed., iii. p. 1146) draws attention to the fact that, as already de Wilde had shown (*Ber.*, vii. p. 353), *in the absence of carbon monoxide* ethylene and its homologues, when mixed with hydrogen and passed over palladium sponge saturated with hydrogen, combine with hydrogen, ethane being formed: $C_2H_4+H_2=C_2H_6$. He believes, however, that benzene also combines with hydrogen, and he proposes calculating the volumes of both from the total decrease of volume, and the specially estimated total value of the heavy hydrocarbons.

Independently of this, Harbeck and Lunge (*Z. anorg. Chem.* 1898, p. 27; *cf.* also Lunge and Akunoff, *ibid.*, 1900, p. 191) equally confirmed the addition of hydrogen to ethylene, but, in opposition to Drehschmidt, they showed that benzene vapour does not combine with hydrogen, which would admit of separating these two groups of hydrocarbons (aliphatic and aromatic) from each other. Unfortunately they had equally to establish the fact that this involves the absence of carbon monoxide — a circumstance not occurring in industrial fuel gases.

It seems to be a fact that the action of bromine and ethylene differs from that on benzene vapour, inasmuch as the former combines with bromine to form the stable compound, $C_2H_4Br_2$, whilst the benzene vapour is removed as a mechanical mixture with bromine, or possibly as a very unstable addition compound, which yields up the bromine to any substance readily reacting with it, such as potassium iodide. On this difference of behaviour, Haber and Oechelhäuser (*J. Gasbeleucht.*, 1900, xliii. p. 347) have founded the following method for estimating ethylene, and indirectly benzene, in coal-gas.

About 90 c.c. of the gas is run into a Bunte burette, the confining water sucked out in the usual manner, and a standard solution of bromine water (about half saturated) allowed to run into the burette up to a definite mark, *e.g.* the 5 c.c. mark, *i.e.*, 15 c.c. of bromine water. A little water is then allowed to enter for clearing the lower capillary tube and the stopcock of bromine water, and the burette shaken for two minutes, after which the colour of bromine vapour should still be distinctly visible. After further three minutes, a concentrated solution of potassium iodide is sucked into the burette, and several times well shaken up. Now the contents of the burette are washed into a beaker, where the liberated iodine is titrated by decinormal thiosulphate solution. For titrating the bromine water, a blank test is made, in which the bromine water is sucked up into the burette up to the same mark as in the other test. The difference of the quantities of thiosulphate consumed in both tests shows the ethylene; 1 c.c. $1/n$ thiosulphate = 1·2 c.c. ethylene at 15° and 760 mm.

The presence of homologues of ethylene does not influence the result, because the number of affinities combining with bromine is the same for equal volumes. But according to Fritzsche (*J. Gasbeleucht.*, 1902, p. 281) industrial gases contain, besides the hydrocarbons of the ethylene series, other constituents absorbing bromine (such as acetylene and its homologues), so that the just-described method, although sufficiently accurate for coal-gas, cannot be applied to oil-gas.

Treadwell (*Lehrbuch*, ii. p. 534) calls Haber and Oechelhäuser's method recommendable in every respect.

In the presence of *benzene* vapour, this, together with the ethylene, is absorbed by fuming sulphuric acid or bromine water, and in a second sample the ethylene is determined by itself as just described.

In the presence of *acetylene*, Tucker and Moody (*J. Amer. Chem. Soc.*, 1901, p. 671) first remove this by an ammoniacal silver solution, before absorbing the ethylene by bromine water.

Fritzsche (*loc. cit.* and *Z. angew. Chem.*, 1896, p. 456) estimates ethylene by treating a somewhat large volume of gas with sulphuric acid, heating in a water-bath, subsequent decomposition of the ethyl-sulphuric acid by boiling with a little water, and determining the alcohol formed by an estimation of specific gravity. That process appears too troublesome for technical purposes. According to this author *butylene* and *ethylene* can be separated by means of sulphuric acid, sp. gr. 1·620, which dissolves only butylene, not ethylene.

An indirect qualitative proof for the presence of ethylene in gas mixtures can also be founded on the fact that, like some other gases and vapours, it interferes with the absorption of oxygen by phosphorus. The percentage of ethylene required for this purpose is stated by various authors from 0·05 up to 0·85. (Details in Czakó's *Beiträge zur Keuntnis natürlicher Gasausströmungen*, 1913, p. 17.) A more sensitive reaction on the presence of ethylene is afforded by absorbing it in a cold saturated solution of mercuric acetate, and setting it free by acidulating the reagent (*ibid.*, p. 19).

BENZENE (BENZOL).

The estimation of this hydrocarbon, together with other "heavy hydrocarbons," *i.e.*, principally the members of the ethylene series, by means of fuming sulphuric acid or bromine water, has been mentioned in several previous places, *e.g.*, pp. 108 and 119. It is, however, very important to ascertain the percentage of benzene vapour by itself, as it is the principal light-giving constituent of coal-gas, its luminosity on burning being about six times that of ethylene.

The estimation of benzene vapour is also of special importance for the "cold carburation" of coal-gas and water-gas, as proposed by Bunte (*J. Gasbeleucht.*, 1893, p. 442), and in the gases of the coking-process by distillation, where benzene is obtained as a commercial product even from poor gases.

We now proceed to the description of the methods for estimating benzene vapour in gases, not yet mentioned in previous chapters, first those of the volumetric, then those of the gravimetric and other classes.

Volumetric Methods.

Hempel and Dennis (*J. Gasbeleucht.*, 1891, p. 414) recommended for the separate absorption and estimation of benzene vapour *strong alcohol* in small quantities. But later on Dennis himself, together with O'Neill (*J. Amer. Chem. Soc.*, 1903, p. 503), proved the unreliability of that absorbent, and recommended instead of it an *ammoniacal solution of nickel nitrate* (16 g. of nickel nitrate, dissolved in 180 c.c. of water + 2 c.c. of concentrated nitric acid, poured into 100 c.c. liquor ammoniæ 0·908). The results are satisfactory, as confirmed by Stavorinus (*Het Gas*, 1905, p. 554). Later on Dennis and McCarthy (*J. Amer. Chem. Soc.*, 1908, p. 233; *J. Gasbeleucht.*, 1908, p. 1534) found that this process only answers in the presence of cyanogen compounds, and they therefore worked out a process founded on the application of an *ammoniacal solution of nickel cyanide*, described *suprà*, p. 108, together with the way of manipulating the apparatus. According to *J. Gasbeleucht.*, 1912, p. 891, this method yields excellent results.

E. Müller (*J. Gasbeleucht.*, 1898, p. 433) absorbs benzene, according to Bunte's proposal by *cooled paraffin oil* of sp. gr. 0·88 to 0·89, boiling about 300°. The gas, dried by calcium chloride, is passed through four absorbing vessels, cooled with ice and salt, placed in series, and connected in such manner that glass touches glass (which, however, as found by Lunge, does not prevent the benzene from being partly absorbed by the india-rubber joints). The current must be slow, say 2 c.c. per second. The absorbed portion is found by reweighing the absorbers, after having taken the temperature of the room; the volume of the non-absorbed portion is measured in a gas-meter. This process is employed at coke works for the estimation of the benzene contained in the gases, which on the large scale is recovered by a precisely similar process.

According to Pfeiffer (Lunge and Berl's *Tech. Chem. Anal.*, iii. p. 277) it is not accurate enough for the analysis of illuminating gas.

As previously mentioned (p. 109) benzene vapour is completely absorbed by *bromine water*. Since it is a fact that benzene, at ordinary temperature, is neither brominated nor oxidised by bromine, it was difficult to understand that the absorption of benzene by bromine should be really complete and quantitative. This was again established by Treadwell and Stokes (*Ber.*, 1888, p. 3131), and confirmed by Haber and Oechelhäuser (*J. Gasbeleucht.*, 1896, p. 804, and xxix. p. 2700). Haber supposed this absorption to be merely a physical process, and this has been confirmed by Korbuly (Inaugural Dissertation, Zurich, 1902). Just as bromine can be removed from an aqueous solution by shaking with benzene, so, *vice versa*, benzene can be removed by shaking with bromine, or even with ethylene bromide, etc.

Nitric acid of the highest degree of concentration (sp. gr. 1·52) also absorbs the benzene, but this process cannot be employed in the presence of carbon monoxide, as this gas is thereby completely oxidised to carbon dioxide, which on removing the acid vapour by caustic potash solution is removed together with the benzene.

Estimation of Benzene in the Form of Dinitrobenzene.—A mixture of fuming nitric acid and concentrated sulphuric acid converts the small quantities of benzene vapour occurring in gaseous mixtures quantitatively into dinitrobenzene, which can be easily traced, as it is little soluble in water, but easily soluble in ether, whilst the products of the reaction of that acid mixture on ethylene are easily soluble in water, and are not extracted by ether. On this behaviour Harbeck and Lunge (*Z. anorg. Chem.*, 1898, p. 41) found a method for the estimation of benzene in the presence of ethylene.

The fifteen-bulb tube K, Fig. 118, is charged with about 110 c.c. of a mixture of equal volumes of concentrated pure sulphuric acid and pure fuming nitric acid, sp. gr. 1·52. After this tube follow the two washing-bottles *h* and *i*, charged with caustic soda solution for retaining acid vapours; then the gas-measuring bottle M, filled with water, closed by a cork with four perforations, put on air-tight by means of sealing wax, through which passes the gas-conduit *g*, the syphon-tube *n* for running out the water, the mercurial pressure gauge *m*, and the thermometer *t*. Tube *n* ends about 20 cm. below the bottom of the bottle in a fine point; tap *q* serves for regulating the outflow into the measuring-flask *v*. Wherever it is unavoidable to employ rubber joints in the parts through which the gas current flows, they must be secured by wire fastenings and painted with a solution of shellac. Wherever the rubber comes into contact with nitric acid vapours, it must be protected on the inside by greasing with vaseline.

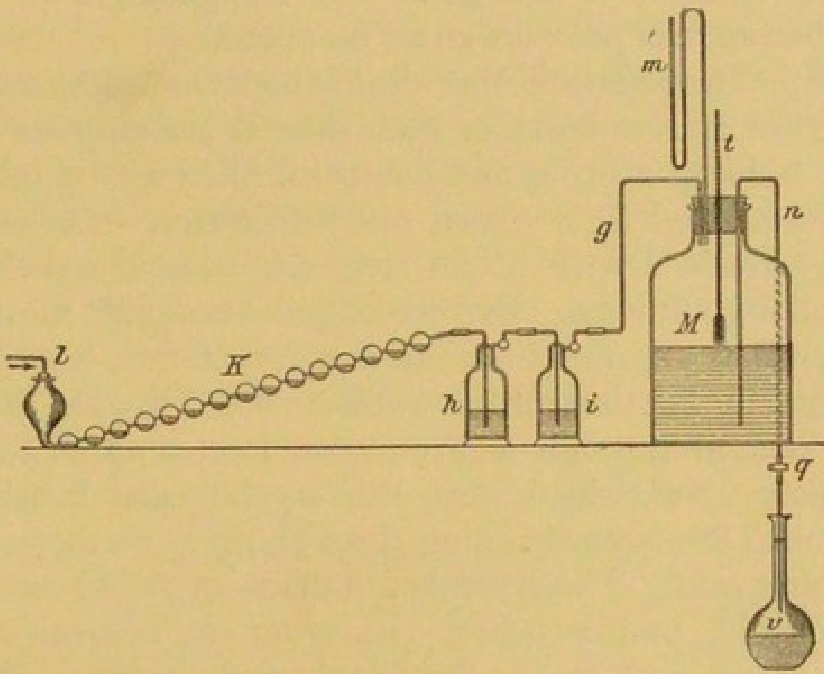

FIG. 118.

The manipulation is as follows:—Before the experiment the air, enclosed in M above the water, is under atmospheric pressure; the column of mercury in both limbs of the gauge-tube *m* must stand at the same level. Now the tube *l* at the other end is connected with the gas-conduit, and the screw clamp *q* is opened so far, that the water in M flows in a thin jet into flask *v*, with a velocity of about 6 litres per hour. The pressure in M must suffer as little change as possible. The running-off water must be measured. Towards the end of the test, when about 200 c.c. less than 10 litres has run out, pinchcock *q* is opened further, so that flask *c* is quickly filled and a little minus-pressure is produced in M. Now *q* is closed, but the introduction of gas is continued, until the pressure gauge *m* again indicates atmospheric pressure. For this purpose the inlet-ends of the tubes in bottles *h* and *i* must be drawn out of the liquid, and the bulb-tube K must be put in a horizontal position. If during the experiment, which goes on for about two hours, the temperature and barometric pressure have not changed, 10 litres of gas have been sent through the apparatus, *plus* the volume of the heavy hydrocarbons retained by the nitrating mixture and the carbon dioxide contained in the gas, which has been absorbed in the washing-bottles, both of which constituents must be estimated in another sample of the gas. The temperature of the gas and the barometric pressure must be noted.

In order to separate the dinitrobenzene retained in the acid mixture, the contents of bulb-tube K are emptied out into a beaker holding 2 litres, and one-third filled with a mixture of ice and water, and K is rinsed out with water. The acid solution is neutralised with about 300 c.c. caustic soda solution (1 : 3), cooling with ice. On prolonged standing, most of the dinitrobenzene separates out as a mass of fine, almost white crystals, partly floating on the surface of the liquid. The clear liquid is poured through a filter, spread on a small aspirating contrivance, upon which also the crystals are brought and washed, until the water running through gives no more reaction on sulphuric acid. The crystals are dried at 70° to 80°, or over sulphuric acid, and weighed. In order to recover also the dinitrobenzene dissolved in the filtrate and washings, the whole liquid is diluted to a round volume, say 2250 c.c.; one-tenth of it, in this instance 225 c.c., is put into a glass-tap bulb, where it is twice shaken up with 50 c.c. ether, ten to fifteen minutes each time. From the united liquids the ether is distilled off in a round-bottomed flask, the last portions of ether and water being removed by a current of air. The residue still contains salts, insoluble in absolute ether. It is taken up with such ether, filtered into a tared glass dish and washed. After evaporating the ether, the previously dissolved quantity of dinitrobenzene is found, multiplied by ten, and added to the principal quantity previously found. From the total quantity of dinitrobenzene, the benzene is calculated by multiplying it with 0·4603.

In order to reduce the weight to volume, we take notice that 1 litre benzene vapour at 0° and 760 mm. pressure weighs

3·5821, measured dry, and that the density of aqueous vapour is equal to one-fortieth of that of benzene vapour. If we denote the temperature of the gas = t, the state of the barometer = b, the tension of aqueous vapour = e, the contents of the gas in volume-per cent. CO_2 and $C_nH_m = s$; the weight of dinitrobenzene = N grammes, the volume of the gaseous remainder in bottle W = W, the percentage of benzene vapour in the gas is:

$$C_6H_6 = 98.505 \frac{N(1 + 0.3665t)(100 - s)}{W\left(b - \frac{31}{40}e\right)} \text{ per cent. by volume.}$$

Pfeiffer (*J. Gasbeleucht.*, 1899, p. 697; *Chem. Zeit.*, 1904, p. 884) points out that in the presence of carbon monoxide this is also partly oxidised by the nitrating mixture. He carries out the dinitrobenzene method, not with a current of gas, but with a certain volume of gas at rest. This allows of dispensing with the cooling by ice, but the product of the reaction must be purified by means of blood-charcoal. The dinitrobenzene is not weighed, on account of the losses in drying, but titrated with stannous chloride by the method of Limpricht (*Ber.*, 1878, p. 35):

$$R.NO_2 + 3SnCl_2 + 6HCl = R.NH_2 + 3SnCl_4 + 2H_2O.$$

The only apparatus for measuring, nitrating, and extraction with ether is a glass tap bulb-tube, with glass stopper, holding ½ litre, the contents of which are exactly measured. Before the experiment, the glass tap and the stopper are moistened with a drop of sulphuric acid. The bulb-tube, after taking out the stopper, is put in a stand, bottom upwards, and is filled from above with the gas to be tested, which after two minutes has driven out the air. The tap is closed, the conducting tube is removed, the tap is opened for a moment in order to make the pressure equal to that of the atmosphere, noting both this and the temperature of the room. Now 2 c.c. of the acid mixture (made of equal parts of concentrated sulphuric acid and strongly fuming nitric acid) is poured into the running-off tube, which still points upwards. By opening the tap, the acid is cautiously run into the bulb up to the last drop, and is made to wet the inner surface all over by repeatedly inclining the bulb. After half an hour the absorption of the benzene is complete. The liquid is again made to moisten all the inner walls of the bulb, 30 c.c. of a concentrated solution of sodium carbonate is rapidly poured in through the mouth of the bulb, and this is shaken until there are no more vapours visible. In case of necessity the neutralisation is finished by adding more sodium carbonate, and at last the liquid is slightly aciduated by hydrochloric acid. No special indicator is needed; the reaction is sufficiently indicated by the change of the colour from orange-red (alkaline) to wine-yellow (acid). By shaking, first of all the excess of carbon dioxide is removed. Then the nitrated product is extracted by twice shaking up with 50 c.c. of ether during five minutes, and placed in a small flask containing 1 g. sharply dried carbonate of potash and 0·5 g. fine blood-charcoal. The mixture which at first shows a strong yellowish red colour, is allowed to stand for several hours, repeatedly shaking it. It is then filtered into a 200 c.c. measuring-flask, rinsed into it with absolute ether, and placed on a water-bath for driving off the solvent. When this has been achieved, about 10 c.c. alcohol and exactly 10 c.c. of a stannous chloride solution (150 g. tin, dissolved in hydrochloric acid, 50 c.c. concentrated hydrochloric acid, diluted with water to 1 litre) is added, and the mixture heated for ten minutes on a water-bath. Now water is put into the flask up to the mark, and 20 c.c. of the mixture (equal to one-tenth) is titrated with decinormal iodine and starch $(=a)$. The stannous-chloride solution is standardised by another experiment, heating 10 c.c. of it with 10 c.c. alcohol in a 200 c.c. flask for ten minutes, diluting up to the mark, and titrating with iodine solution $(=b)$. The difference $b-a$ shows the consumption of iodine for the dinitrobenzene, whose weight is:

$$= (b-a)10 \times 0{\cdot}0014 \text{ g.}$$

The calculation of the weight of dinitrobenzene for volume-per cent. of benzene vapour in the illuminating gas examined is based on the following data:—1 g. dinitrobenzene = 0·4643 g. benzene; 1 g. benzene = 279·2 c.c. vapour at 0° and 760 mm. pressure. If we denote the weight of the dinitrobenzene ascertained as above, g, and the volume of gas employed (*i.e.*, the contents of the bulb-funnel J), the percentage in volume of benzene vapour in the gas is:

$$g \times 0{\cdot}4643 \times 279{\cdot}2 \frac{(273+t)760}{273b} \times \frac{100}{J} = \frac{36090}{J} \times g \times \frac{273+t}{b}.$$

(In the place of the quotient 36090 : J, of course, a constant magnitude for the bulb-funnel employed may be introduced.)

According to the analyses quoted by Pfeiffer, this method yields results sufficiently in accordance with those obtained by the Harbeck-Lunge method, and the nickel nitrate method of Dennis and O'Neill (*suprà*, p. 289).

Estimation of Benzene Vapour by Freezing.

H. Ste. Claire Deville (*J. Gasbeleucht.*, 1889, p. 652) proposed separating the benzene from gaseous mixtures by cooling down to a constant temperature of -22° C., and weighing the crystallised benzene. The weight thus found must be increased by 23·5 g. benzene per 1 cb.m. gas, which quantity remains in the gas, cooled down to -22°. The condensed benzene is taken up in the glass serpentine coil, shown in Fig. 119, about 7 mm. wide inside, closed by rubber stoppers and weighed before the experiment. It is then placed in a freezing-mixture, as shown in Fig. 120, contained in a thick-walled vessel, provided with an outlet at the bottom for water dropping out. The freezing-mixture consists of 3 litres crushed ice and 0·6 litre cattle-salt. A thermometer placed in the same vesse ought to show a pretty constant temperature of -22°.

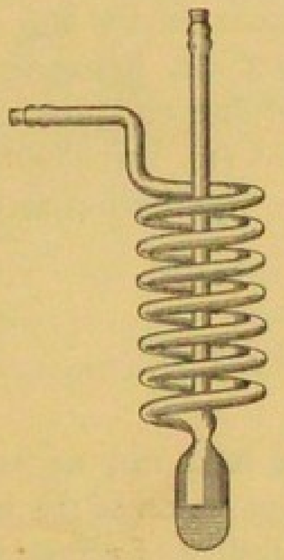

FIG. 119.

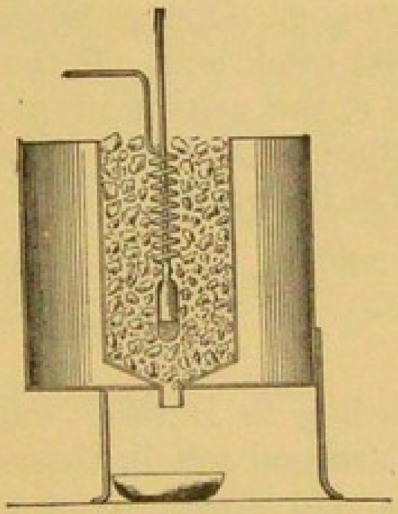

FIG. 120.

Before introducing the gas into the serpentine coil, it must be well dried in a calcium-chloride tower. The connection with the coil is made by a very short rubber tube. Behind the apparatus is placed a gas-meter for measuring the gas passed through, with a thermometer; the temperature should be again that of the room. The benzene separates in the coil in a solid form. If this should cause the coil to be stopped up, it must be carefully taken out of the freezing-mixture and for a moment placed in water, so that the benzene fuses and collects in the bulb below the coil; after this the passage of the gas through the cooled coil can go again. The experiment should be kept going on for six or eight hours, at the rate of 150 litres gas per hour. Then the coil, again closed by the rubber stoppers, is weighed, the increase of weight indicating the quantity of benzene separated from the gas. This quantity is calculated upon 1 cb.m. gas, and increased by the constant figure 23·5 g. One g. benzene = 279·2 c.c. benzene vapour at normal conditions. If the weight of the condensed benzol is put $= g$, the volume of gas employed (in litres) $= V_1$, t its temperature and b the pressure, the volume-percentage of benzene in the gas is:

$$\left(\frac{g \times 1000(273+t)760}{V_1 \times 273b} + 23{\cdot}5\right)0{\cdot}02791.$$

According to Deville's experiments, it is not necessary to employ a second coil for the complete separation of the benzene. An advantage of the process is the possibility of examining the quality of the condensed product by distillation, but the method is too troublesome for checking the daily work.

Calculation of the Amount of Benzene Vapour from the Specific Gravity.

Pfeiffer (Lunge and Berl's *Untersuchungsmethoden*, iii. p. 275) makes an approximate estimation of the benzene vapour in coal-gas from its specific gravity, and the total quantity of heavy hydrocarbons, C_nH_m, present in the gas. First, from the total analysis and the experimentally determined specific gravity of the gas, the specific gravity of the heavy hydrocarbons, C_nH_m, is calculated by the rules given in a previous chapter (p. 179). We further take notice that according to series α the specific gravities β are as follows:—

	α.		β.
a. Ethylene (C_2H_4) . Propylene (C_3H_6) .	0·9674 1·4550	$\}C_nH_{2n}$ . .	1·0689
b. Benzene (C_6H_6) . Toluene (C_7H_8) .	2·7041 3·1875	$\}C_nH_{2n-6}$.	2·8008

Experience has shown that in coal-gas the higher homologues of the groups *a* and *b* are only present in very small proportions; we assume here that they amount to about one-fifth of the fundamental substance, which leads to calculating the average specific gravities of the two groups C_nH_{2n} and C_nH_{2n-6}, as stated *sub* β. Mixtures of the two groups will hence possess an average specific gravity, which is always between the two limits 1·0 and 2·8; it will be nearer one or the other of these values, the more the gases or vapours of the corresponding groups are present. Quite generally the volumes of the two groups will be in inverse proportion to one another, as the differences of their specific gravities against the calculated specific gravity s of the mixture C_nH_m:

$$C_nH_{2n} : C_nH_{2n-6} = (2{\cdot}8 - s) : (s - 1{\cdot}0).$$

Hence the contents of benzene vapour in each $(2{\cdot}8 - s) + (s - 1{\cdot}0)$ volumes of heavy hydrocarbons is $= (s - 1{\cdot}0)$ volumes, and in the total quantity of heavy hydrocarbons

$$(C_nH_m) = \frac{(s - 1.0)C_nH_m}{(2.8 - s) + (s - 1.0)} = \frac{(s - 1.0)C_nH_m}{1.8}$$

per cent. benzene by volume.

Let us suppose, for instance, that we have 3·7 per cent. heavy hydrocarbons (C_nH_m), and their specific gravity s calculated = 1·7939; from this follows, according to the formula just given, benzene vapour = 1·6 per cent. and ethylene = 2·1 per cent.

The experiments made by Pfeiffer showed that, in spite of some objections which might be made against the above-described estimation of benzene by calculation, in the case of illuminating gas the results agree very well with those of the best methods for estimating the benzene. But of course that way will be only taken, if the data for the calculation need not be specially ascertained for this purpose, but can be occasionally used.

An apparatus for the estimation of benzene in coal-gas founded on passing the gas through a known quantity of benzene up to saturation, is described in the Ger. P. 267491 of the Société Roubaisienne d'Eclairage par le Gaz, and R. R. L. H. Forrières.

General Remarks concerning the Estimation of Benzene Vapour in Gases.

Benzene vapour is very sensibly absorbed by water and by all aqueous solutions of salts. Treadwell (*Lehrbuch*, ii. p. 532) quotes special experiments made in that respect by Korbuly, with water and caustic potash solution. When analysing gases containing carbon dioxide and benzene, always first the CO_2 is absorbed by caustic potash, and subsequently the benzene by fuming sulphuric acid or bromine water. But both estimations will be wrong, if fresh caustic potash solution is employed for absorbing the CO_2, for it will not merely absorb the whole of the CO_2, but also very much, possibly nearly all the C_6H_6. The results are only to be trusted if the caustic solution is previously saturated with benzene, which will be the case after prolonged use.

This objection, of course, does not apply to the special methods for the estimation of benzene, described in the present chapter, which are applied to large quantities of gas, *not* previously treated with caustic liquor or other aqueous solutions.

NAPHTHALENE VAPOUR.

Although most of the large quantities of naphthalene produced from the coal during its distillation is condensed in the tar, yet the small quantity of naphthalene vapour left in the purified gas (which rarely exceeds 15 or 20 grains per cubic foot) frequently causes great trouble by depositing in the solid state in the gas mains. This had led to applying special methods for removing the naphthalene from the crude gas by washing or cooling, and its estimation in the gas is therefore useful for testing the working of such apparatus.

No satisfactory method is as yet known for estimating the amount of naphthalene present in the gas still containing tar owing to the difficulty of separating the tar-fog, without at the same time removing part of the naphthalene present as vapour; but for the cooled gas free from tar-fog, several methods are used, all of which depend on the fact that naphthalene combines with picric acid to form the crystalline picrate, $C_{10}H_8 . C_6H_3N_3O_7$, fusing at 147°, which is practically insoluble in picric acid solution, although it is partly dissociated into its constituents by water. This way of estimating the naphthalene has been, *e.g.*, employed by Küster (*Ber.*, 1894, p. 1101).

Colman and Smith (*J. Soc. Chem. Ind.*, 1900, p. 128) pass the gas through a series of three absorbing bottles, charged with a nearly saturated solution of picric acid in water, about one-twentieth normal, of which 100 c.c. is used in the first, and 50 c.c. in each of the other two bottles. The gas is first passed through a bottle charged with citric acid solution, to remove ammonia, which would otherwise neutralise some of the picric acid, and then bubbled through the latter at the rate of ½ to 1 cb. ft. per hour, until 10 to 15 cb. ft. have passed through. The whole of the naphthalene is thus taken out of the gas (already the first bottle removes all but traces) and separates as naphthalene picrate, which, however, undergoes a partial dissociation into free naphthalene and picric acid. To effect the complete conversion of the naphthalene into picrate, the method of Küster (*loc. cit.*) is followed. According to this the contents of the absorption bottles are washed with as small a quantity of water as possible into a narrow-mouthed bottle of such size that it is nearly filled with the liquid; this bottle is then closed by a rubber cork, through which passes a glass tube, closed at the lower end, but having a small hole blown in the side about 1 in. from the bottom. The tube is placed so that this hole is just below the bottom of the stopper, and the bottle then evacuated as completely as possible with a water-jet pump; whilst the pump is still working, the tube is raised so that the small hole is well above the bottom of the stopper, the bottle being thus sealed. It is then placed in a water-bath containing sufficient water to cover it, the water heated to the boiling-point, and the heating continued until the liquid is quite clear. The bottle is then allowed to cool, with occasional shaking to wash down any naphthalene sublimed into its upper portion. After standing overnight, the naphthalene picrate is separated completely and is filtered off on the pump, and the precipitate washed with a small quantity of water. When too much water is used, the results are too low. It is therefore preferable to pour the contents of the bottle into a measuring cylinder, and note the volume; then to filter through a dry filter-paper, rejecting the first few cubic centimetres of filtrate, and to titrate 100 c.c. of the filtrate with $n/10$ potassium hydroxide. The indicator may be phenolphthalein or lacmoid, or methyl orange. If n = volume in cubic centimetres of the liquid after heating, and v the number of cubic centimetres of decinormal alkali required for 100 c.c. of the filtrate, the volume of decinormal alkali required for the whole solution is $\frac{n \times v}{100} = V$. The alkali equivalent of 100 c.c. of picric acid solution originally used, called V^1, is ascertained by titration with decinormal alkali in a similar manner, and the difference between $V^1 - V$ shows the quantity of decinormal alkali corresponding to the picric acid removed by combination with naphthalene. One c.c. of decinormal alkali corresponds to 0·0229 g. of picric acid, and therefore to 0·0128 g. or 0·1975 grain of naphthalene, as 229 parts of picric acid combine with 128 parts of naphthalene. The number of grains of naphthalene per 100 cb. ft. is:

$$\frac{(V^1 - V) \times 100 \times 0.1975}{\text{Volume of gas present}} = \text{grains } C_{10}H_8 \text{ per 100 cb. ft.}$$

Pfeiffer (Lunge and Berl's *Untersuchungsmethoden*, iii. p. 304) proceeds as follows:—He employs a Pettenkofer tube, 30 cm. long and 2 cm. wide, charged with 15 c.c. of picric acid solution, prepared by dissolving 15 g. picric acid in 2 litres water, and filtering after complete cooling. In order to avoid the evaporation of water from this liquid, and at the same time to retain the last traces of ammonia, it is imperative to place between the gas-tap and the Pettenkofer tube a Peligot tube, charged with 10 c.c. decinormal acid. This last tube must have ground-in glass connections; any rubber connections up to the absorption tube should be avoided as much as possible, as they absorb much naphthalene. Where they cannot be avoided, the ends of the glass tubes must be made to touch each other, the connection being made with strongly charged old rubber tube. The gas is measured by a meter behind the washing-apparatus; it should pass through at the rate of 20 to 25 litres per hour, and in the whole 150 litres should be used. When the experiment is finished, the absorbing liquid (without heating it, as prescribed by Colman and Smith; this is quite unnecessary) is separated from the crystallised picrate by filtration through cotton-wool, and 15 c.c. of the filtrate titrated with $N/50$ caustic potash and a drop of methyl orange solution. The final reaction is easily recognised with good light and on a white background, if you look at the drops as they fall in, not at the mixture. The standard of the original absorbing solution is established by titration in the same manner. Example: Quantity of gas employed, 168 litres; titre of 10 c.c. picric acid solution = 21·9 c.c. of $N/50$ KOH; the same of 10 c.c. filtrate after the absorption = 15·6 c.c. $N/50$ KOH. Hence consumed $21{\cdot}9-15{\cdot}6=6{\cdot}3$ c.c. $N/50$ KOH, and for the 15 c.c. absorbing liquid, $6{\cdot}3\times1{\cdot}5=9{\cdot}45$ c.c. $N/50$ KOH. Since 1 c.c.$=0{\cdot}00256$ $C_{10}H_8$, the 100 cb.m. gas contain $\frac{9{\cdot}45}{168}\times256=14{\cdot}4$ g. $C_{10}H_8$.

Jorissen and Rutten (*J. Soc. Chem. Ind.*, 1909, p. 1179) point out that the process of Colman and Smith (*suprà*, p. 299) yields low results, if too much water is used in washing the naphthalene picrate; further, that, by employing a saturated solution of picric acid containing also solid picric acid, the naphthalene picrate is directly precipitated from the gas as undissociated picrate. They proceed as follows: 250 c.c. of a saturated solution of picric acid are evaporated to about 150 c.c. and transferred, while hot, to two absorption bottles. The gas, previously freed from tar-fog, cyanogen, sulphuretted hydrogen and ammonia, is passed through the bottles at the rate of about 1·5 cb. ft. per hour, until a fair quantity of picrate has been formed in the first bottle. The solution and precipitate are then washed into a flask, made up to 250 c.c., the closed flask heated to about 40° for about half an hour, and shaken from time to time till all the picrate has dissolved. After cooling, the solution is separated from the precipitated naphthalene picrate, and an aliquot portion of the filtrate titrated with *N*/10 alkali, the same volume of the original solution being also titrated. From the difference of the two titrations the amount of naphthalene is readily calculated in a similar manner to that given above.

Schlumberger's description of Rutten's method in *J. Gasbeleucht.*, 1912, p. 1260, substantially agrees with the method described by Pfeiffer *suprà;* it is there pointed out that the standardising of the picric acid, in lieu of alkalimetrical titration, may be conveniently performed by a solution of 150 g. potassium iodide and 30 g. potassium iodate in 400 c.c. water, with starch solution as indicator; 1 mol. $C_{10}H_8$ combines with 1 mol. of picric acid. Benzene vapour is *not* absorbed by cold saturated picric acid solution.

Albrecht and Müller (*J. Gasbeleucht.*, 1911, p. 592) modify the above-described method by not evaporating a cold saturated picric acid solution, but preparing a saturated solution containing an excess of solid acid by employing 2·5 picric acid, together with a quantity of water insufficient for dissolving it, divided upon two wash-bottles. When estimating the naphthalene in *crude* gas, the gas must not be purified otherwise than by sulphuric acid and caustic potash solution, since all solid purifying agents retain naphthalene and cause the results to be too low.

Pfeiffer (*loc. cit.*, p. 305), to prevent the error caused by naphthalene being separated together with the tar condensing in the conduits before the absorbing apparatus, proceeds as follows:—A ¾-in. tap is put in the gas-conduit, through which passes a glass tube, movable in a rubber stopper, one end of which enters freely in the gas-pipe. The other, outer end is connected with a pipe, filled with cotton-wool for retaining tar-fog. Then follow three Peligot tubes with glass joints. The first two are charged each with 100 to 200 c.c. of 66 per cent. acetic acid, the last with a concentrated picric-acid solution. A gas-meter follows in the end. After passing about 150 litres gas through the apparatus in five or six hours, the whole apparatus, beginning at the gas-conduit up to the last Peligot tube, without taking it to pieces, is taken to the laboratory, in order to drive all the naphthalene into the absorbing vessels. This is done by sucking a current of air through the apparatus and heating the gas-inlet pipe, together with the cotton-wool filter, on a steam-bath, whilst cooling the Peligot tubes with water; this takes about an hour. Now the contents of the three Peligot washers are united and mixed with another 500 c.c. concentrated picric acid solution, whereby all the naphthalene is precipitated in flakes. It is filtered through an aspirating funnel, dried in vacuo and weighed; 1 g. picrate = 0·3585 $C_{10}H_8$. In this way Pfeiffer obtained from crude gas 0·308 g. picrate = 110·4 g. $C_{10}H_8$ in 100 cb.m. of gas.

C. J. Dickenson Gair (*eodom loco*, 1905, p. 1279; 1907, p. 1263) passes the gas through two absorption bottles containing 350 c.c. of diluted acetic acid of sp. gr. 1·044, at the rate of 1 cb. ft. per hour. At the conclusion of the test, 500 c.c. of saturated picric acid solution are added, the dissolved naphthalene being thereby precipitated as picrate, which is filtered off on the pump, using a dry, weighed filter washed with saturated picric acid solution, and finally once with water. The filter-paper and precipitate are dried quickly in vacuo over sulphuric acid, and weighed. The weight of the naphthalene picrate found, multiplied by $\frac{128}{128+229} = 0{\cdot}3585$, gives the weight of naphthalene in the volume of gas passed. Or, the precipitate may be washed into a flask, and titrated in hot solution with *N*/10 alkali, as previously described. In the case of cool, but unpurified gas containing HCN and H_2S, those impurities are apt to affect the picric acid to some extent; in this case the absorption by acetic acid is preferable.

The employment of alcohol to wash the naphthalene from the gas and subsequent precipitation of the solution with aqueous picric acid has not proved successful, as under these conditions some of the other vapours present in the gas, such as the xylenes, also form crystalline picrates, and too high results are therefore obtained. Still, this process is recommended by Ab-der-Halden, *J. Gas Lighting*, cxx. p. 230.

Fronsac (*Rév. gén. de chim.*, 1914, p. 4) describes a wash-bottle specially constructed for the picric acid method.

Laurain (*Bull. Assoc. Belg. des Chim.*, 1912, No. 1; *J. Gas Lighting*, 1912, cxviii. p. 984) describes the method of Sainte-Claire Deville for separating the naphthalene by cooling in a glass tower containing a copper spiral, through which circulates water of 2° or 3° C. The naphthalene condensed in the upper part of this tower is dissolved in alcohol, precipitated by water from the solution, filtered, dried, and weighed, adding the quantity remaining in the state of vapour at the temperature of the cooling water. This method is rather difficult to carry out in a satisfactory manner.

Another method, worked out by Laurain himself, ascertains the temperature at which the naphthalene separates from the gas in a solid form, and measures the loss of pressure produced by this secretion, with tables reducing this to the percentage of naphthalene.

Lebeau and Damiens, in a number of communications made in 1913 (*Comptes rend.*, clvi. and clvii.), describe their methods for the examination of hydrocarbon mixtures by the application of low temperatures.

The Société du Gaz de Paris (Ger. P. 266154) estimates the percentage of naphthalene in illuminating gas by the temperature of saturation of the naphthalene vapour, by means of an apparatus provided with a contrivance for regulating and measuring the temperature, consisting in a narrow orifice in the gas-pipe, in which a differential manometer measures the diminution of pressure. The gas is introduced at the ordinary temperature, so that the thermometer shows the temperature at which in the orifice (which may be still further narrowed by an artificial deposition of naphthalene) no naphthalene is either precipitated or evaporated.

TOTAL HEAVY HYDROCARBONS IN COAL-GAS.

Their estimation by absorption in concentrated sulphuric acid or bromine water has been described *suprà*, pp. 118 and 119). Hempel and Dennis (*Ber.*, 1891, p. 1162) pass the gas first into a Hempel burette where it is measured, and from this into a gas-pipette filled with mercury, say an "explosion-pipette" (pp. 90 and 156), where it is shaken up for three minutes with 1 c.c. of absolute alcohol, which takes out all the hydrocarbon vapours. The gas is carried back into the burette, and from this, in order to remove the alcohol vapour, into a second mercury pipette, where it is shaken up with 1 c.c. of water for three minutes, after which the contraction of volume is noted. Both alcohol and water should first be saturated with coal-gas to prevent methane, carbon monoxide and nitrogen from being dissolved, as specially pointed out by F. Fischer (*Z. angew. Chem.*, 1897, p. 351).

Bujard (*Z. angew. Chem.*, 1897, p. 45) recommends this method, both for coal-gas (for which he also employs 1 c.c. alcohol) and for "air-gas," for which 4 or 5 c.c. alcohol should be taken.

Merriam and Birchby (*J. Ind. and Eng. Chem.*, 1913, p. 822) describe their empirical tests for approximately determining the quantity of gasoline obtainable from natural gas, viz., absorption by kerosene and by olive oil. They got the best results by compressing the gas in a compressor constructed by them.

James G. Vail (*J. Ind. and Eng. Chem.*, 1913, p. 756) estimates the hydrocarbons in coal-gas, after absorbing CO_2, CO, and O, by explosion with a mixture of O and N, prepared in the pipette itself by the electrolysis of water acidulated with sulphuric acid.

TAR VAPOURS.

Most of the tar produced in the distillation of coal is condensed to a liquid already in the hydraulic main in the condensers, and the Pelouze or Livesey apparatus, specially constructed for this purpose. Still, even in the normal working of the best apparatus, the finest tar-fog is carried forward by the gas; it passes partly through the scrubbers, and almost the last traces of it are ultimately retained in the oxide-of-iron, purifying mass, owing to its filtering action. This is certainly not the proper object of that mass, which by its becoming soaked with tar is prematurely rendered useless for its proper task in the manufacture of gas, and, moreover, later on causes great trouble in working the mass for cyanides, etc. The *crude gas* ought to be freed from tar as much as possible in the condensers and scrubbers before it goes into the purifiers. Hence the examination of the *crude gas* for its contents of tar in that particular place gives valuable information on the working of the process. The *street gas* also always contains traces of tar vapours, which impart to it its specific smell; but these traces are so slight that they cannot be supposed to do any harm, and therefore they need not be specially enquired into. To be sure Freitag (*J., Gasbeleucht.*, 1870, p. 33) attributes the damage done to plants in the case of gas issuing from leaks in the gas-pipes, just to the tar vapours; *cf.* also Pfeiffer (*ibid.*, 1898, p. 137).

The *qualitative* proof for the presence of tar vapour in *crude* gas is generally made by placing a piece of white paper against the gas issuing from a small orifice. The place struck by the gas in front of the scrubbers at once turns brown or black, behind the washer only after some time.

In *street gas* any tar present can be proved by a solution of a small crystal of diazobenzene-sulphuric acid, dissolved in 10 c.c. water (Pfeiffer, in Lunge-Berl's *Chemisch-technische Untersuchungsmethoden*, iii. p. 307).

The *quantitative estimation* of tar-fog in the gas is carried out by various methods.

1. Tieftrunk's apparatus (Fig. 121) causes the gas to pass through spirit of wine which mechanically retains the tar; the latter is estimated by filtration and drying. The absorbing-cylinder *a* is provided at the top with a brass flange, with which the ground-up brass cover *b*, greased with a little tallow, is connected air-tight by the screw clamps *k*, *k*. The gas goes in through pipe *e*, which is continued by means of rubber tubes with tube *g*, reading nearly down to the bottom of *a*. Tube *g* carries six loosely put on brass bells, perforated with a number of 1·5 mm. holes, in distances of 5 mm. Alcohol of 30 to 35 vols. per cent. is put into *a* so far that all the bells are covered. On the gas passing through the holes, the tar-fog is mechanically retained,

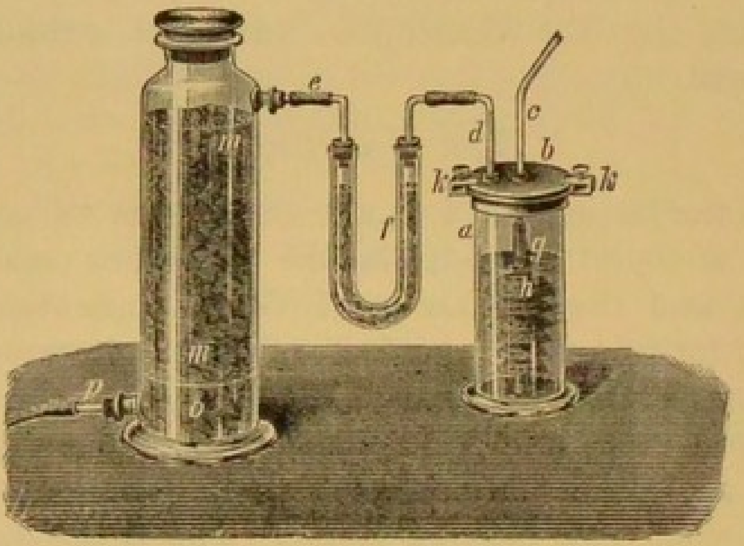

FIG. 121.

and the last traces of it are kept back by the cotton-wool, loosely filling the U-tube *f*. The tubulated bottle now following contains at the bottom a layer of India fibre *o*, above this a disc of filtering-paper, and on this a layer of bog-iron ore purifying-mass, intended to retain the sulphuretted hydrogen which would damage the meter. The gas gets out through *p*, its propulsion through the apparatus being produced by a water-jet pump.

This apparatus, if possible, is placed close to the orifice for the gas; if this is not possible, it is connected with it by a tared glass pipe, inclined towards the apparatus, which is reweighed after finishing the test. In front of the condensers, 250 litres gas are drawn through the apparatus with a velocity of 30 to 40 litres per hour; in front of and behind the scrubbers 500 litres with a velocity of 50 to 60 litres per hour.

After finishing the passage of gas, cover *b* is removed, the tar adhering to the bells washed off with alcohol of 30 to 35 vols. per cent., and the washings poured to the liquid remaining in the vessel. After twelve hours' settling, the liquid is passed through a dry, weighed filter by the aid of an air-pump, which is stopped as soon as the tar gets on to the filter. The alcoholic liquid is allowed to drain off, the filter and contents are put into a tared glass dish, which is placed into a desiccator for twelve hours and weighed. The cotton-wool in tube *f*, if coloured, is washed with carbon disulphide. The filtrate is allowed to drop into a tared glass dish, which is dried at the ordinary temperature in a current of air. The weight of the remaining tar is added to that found before. Since a little tar has remained in the bottle *a* and on the bells, dry air is sucked through the bottle until all the moisture has vanished, and the increase of weight of the (previously weighed) apparatus is noticed. The balance used must, when weighed with 1 kg., indicate 0·01 g. The results are noted in terms of kilograms tar per 1000 cb.m. gas. In that quantity, 150 to 200 kg. tar are found in front of the coolers, 25 to 75 kg. in front of the scrubbers, 0·5 to 20 kg. in front of the purifiers.

Tieftrunk's method is very strongly criticised by Feld, in his paper quoted below, as yielding quite unreliable results.

2. Clayton and Skirrow (*J. Gas Lighting*, 1907, p. 660) retain the tar-fog by a cotton-wool filter. A long glass tube, ¾ in.

in external diameter, has a small hole, ¼ in. diameter. Down near one end, and about 12 in. of the tube above this hole is filled with loosely packed cotton-wool, which has been previously extracted with carbon disulphide to remove fatty matter. The end of the tube near the small side hole is closed by a cork; the tube inserted through a cork is placed in a 1½-in. cock on the gas main, and so fixed that the small side hole faces the gas stream as nearly as possible two-thirds across the main, or one-third of the diameter from the side opposite to the cock through which it is inserted, this being the point of mean velocity of gas in the main. The whole of the filtering material should be within the main, so that it is kept at the same temperature as the gas to avoid condensation, and the gas is allowed to pass through the filter at such a rate that its velocity through the ¼-in. hole is greater than that of the gas in the main. Only by observing these precautions uniform results can be obtained. After passing the filter, the gas is purified from sulphuretted hydrogen by oxide of iron, and measured in a meter, from 20 to 30 cb. ft. being employed. The tube is then removed from the main, the external surface wiped clean from tar, and the cotton-wool containing the tar placed in a Soxhlet tube and extracted with carbon disulphide in a tared flask. The CS_2-extract is evaporated on a water-bath, dry air finally drawn through the flask for half a minute, and the flask again weighed. From the weight of tar and the volume of gas passed, the amount of tar-fog per 1 or 100 cb. ft. of gas is readily calculated. The free carbon of the tar remains undissolved in the cotton-wool, and some of the low-boiling constituents of the tar are evaporated with the carbon disulphide, so that the results are below the exact figure; but the figures obtained are fairly comparative and sufficiently exact for most practical purposes.

Feld (*J. Gasbeleucht.*, 1911, p. 33) tries to avoid the just-mentioned errors of this method in the following manner:—The gas drawn from the main is passed through a weighed U-tube containing cotton-wool. Before weighing, the latter is placed in a water-bath warmed to the temperature of the gas in the main, and the gas passed through it, after traversing two additional U-tubes placed in the same bath and filled with cotton-wool (unweighed) and calcium chloride respectively, until its weight is constant. The tube is then connected directly with the tar-laden gas stream, and a measured volume of gas passed through it. It is then reconnected to the outlet of the two U-tubes previously employed, and the gas again passed until the weight of the tar absorption tube is constant; the increase of weight gives the amount of tar-fog in the volume of gas passed. Working in this manner, the moisture in the filtered tar is removed without simultaneous loss of tar vapours, as the gas is always saturated with tar vapours at the temperature of the water in the bath and in the gas main. By lowering the temperature of the bath, the lowering of the tar contents of the gas for any interval of temperature can be determined.

Gwiggner (*Chem. Zeit.*, 1912, p. 461) retains the tar by a slag-wool filter.

Jenkner (*Stahl u. Eisen*, xxxii. p. 1129; *Chem. Centr.*, 1912, ii. p. 1498) describes an apparatus for discovering tar, ammonia, and benzene in coke-oven gases, in which the tarry constituents are retained on a cotton-wool filter, heated to 65° to 70° by electrical means. The ammonia is removed by blowing pre-heated air through the filter.

DETECTION OF INFLAMMABLE GASES AND VAPOURS IN THE AIR.[1]

In some cases the air contained in a closed space, *e.g.*, in the bunkers of coal-ships, benzene tanks, oil-ships, etc., should be regularly tested for the presence of inflammable gases and vapours. For this purpose an automatically acting apparatus has been constructed by Philip and Steele (*J. Soc. Chem. Ind.*, 1911, p. 867) which depends, like some others previously devised, upon the catalytic action of heated platinum surfaces to secure the combustion of mixtures of oxygen and combustible gas or vapour which may be passed through it; but, differently from its predecessors, is so arranged that it is completely guarded against any danger of overheating whatever the proportion and nature of the mixture of combustible gas and vapour with air may be.

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[1] *Cf.* Lunge-Keane's *Technical Methods*, i. pp. 896 *et seq.*, and *suprà*, p. 152.

Their detector, Fig. 122, consists of two coils of platinum wire, C_1 and C_2, of approximately the same resistance and arranged parallel with one another. In series with each of them is one of the coils of a differential galvanometer, G_1 and G_2, in fact, a relay. The armature or relay tongue *t* (Fig. 123) of this relay is capable of being moved by a very small strength of the current flowing in either of its coils. The two platinum coils of the detector are enclosed in glass tubes, and the gas which is to be examined is pumped over the outside of one of these tubes enclosing the coil C_2, without coming into contact with the platinum wire. The gas current then passes on to the second glass tube inside which it flows, and is thus brought directly into contact with the hot platinum coil C_1. Connected in series between each of the platinum wire coils, C_1 and C_2, and the coils of the relay, G_1 and G_2, to which they are joined, is a small low-resistance annunciator coil. These two coils are marked A_1 and A_2 in Fig. 122. When the switch of the apparatus is closed, they indicate visually whether the currents

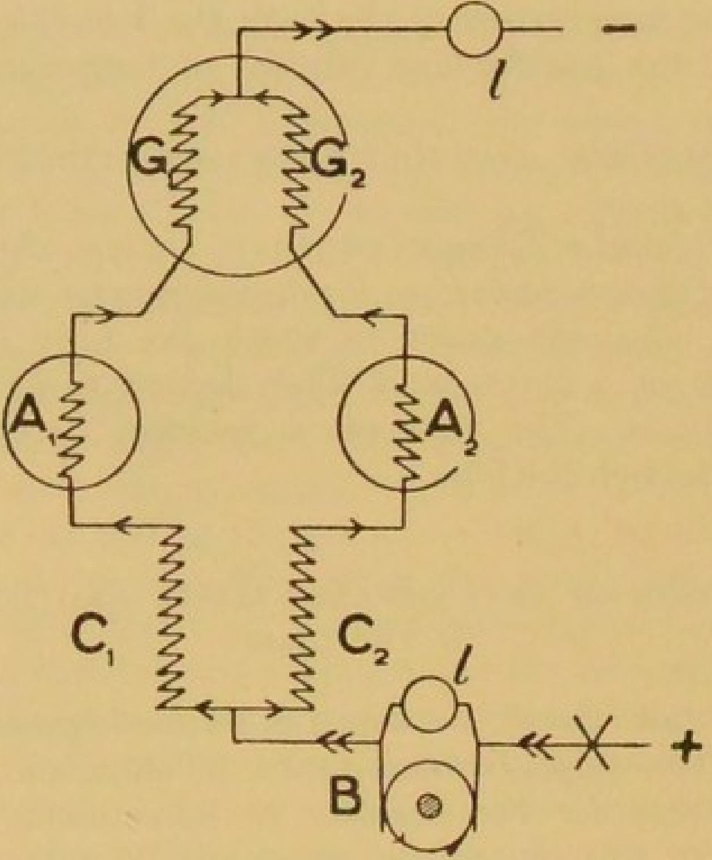

FIG. 122.

are actually passing through both of the platinum coils. In the event of either of these being fused or broken, the corresponding annunciator shows a red spot, marked "right" or "left-hand platinum coil fused." On the other hand, if the coils are carrying the correct currents, each annunciator shows the letters O.K.

The electric currents of the relay, which are quite separate from those of the electric coil circuit, are for the sake of simplicity not shown in Fig. 122, but are shown separately in a diagrammatic form in Fig. 123. In this diagram the relay tongue *t* moves between two stops S_1 and S_2, and is itself connected to a point between two electric incandescent carbon filament lamps, marked R and W. These two lamps are arranged in series across the supply mains to which the detector is connected. One lamp, R, is contained in a red glass, and the other, W, in a colourless glass shade. It is evident that when the relay tongue is against either of the stops S_1 or S_2, the corresponding lamp is short-circuited through the stop and relay tongue, and is therefore extinguished, whilst the other lamp has the full voltage of the supply mains on it, and is consequently burning at full brightness. In the diagram, Fig. 123, the red light R is short-circuited, and the white lamp W is lighted. This is the normal condition of the detector when connected to the mains, if the air under test contains no inflammable gas or vapour.

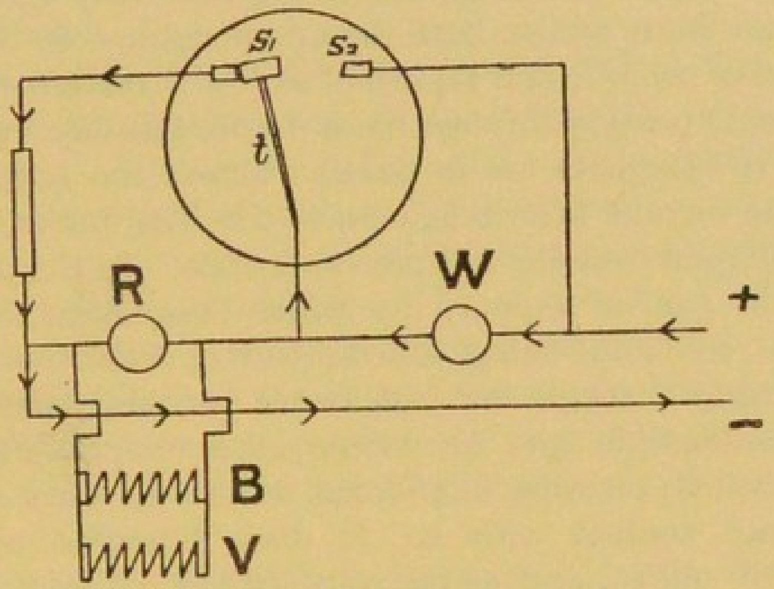

FIG. 123.

Let us suppose that the instrument is connected to the mains, then a current of electricity flows through the series of coils C_1, A_1, G_1 (Fig. 122), and another of approximately the same strength through the series C_2, A_2, G_2. If the relay tongue is then properly adjusted for these particular current strengths, it will rest as shown in Fig. 123, so that the white lamp W is burning and the red lamp R is extinguished, whilst the annunciators A_1 and A_2 will show O.K. The current passing through the coils C_1 and C_2 is so strong that they scorch paper held against them, whilst both the annunciator coils A_1 and A_2, and the relay coils G_1 and G_2 are of so low a resistance that the same currents passing through them do not sensibly warm them.

As all the currents are in parallel across the supply mains, directly the current is switched on to the instrument, a current of air is pumped over the hot platinum coils. In the absence of combustible gas or vapour, the white lamp remains lighted, whilst the red lamp, being short-circuited, shows no light. If the air passing through the instrument becomes contaminated with a combustible gas or vapour, the temperature of the platinum coil C_2 remains unaffected, as the air does not come directly into contact with it. It does, however, come into contact with coil C_1, and as the combustible material burns by the catalytic action of the surface of the hot platinum, it further heats the wire to a degree corresponding with the amount of inflammable gas or vapour in the air. Owing to this, the resistance of coil C_1 rises, and this causes a diminution of the current flowing through the relay G_1. This causes the release of the relay tongue, and it therefore swings against the other stop S_2. This action breaks the short circuit of the red lamp, which becomes lighted, whilst the white lamp is at the same time short-circuited and thus extinguished, and by this means a visual signal is given that a definite percentage of inflammable gas or vapour is present in the air under test. In parallel with the red signal lamp and with one another are arranged two other circuits, viz., a single-stroke electric bell B, and secondly, a valve-coil V. These, however, may be arranged as in the instrument shown here in series with each other, and in parallel with the red signalling lamp. The bell coil may be installed at any suitable distant point. The valve coil actuates a gas cut-off valve.

The original communication contains a number of further devices for making the action of the instrument safe and more sensitive. It was testified in the discussion following the reading of this paper that the instrument was doing very good service, and retained its efficiency for years.

Various patents of the same inventors (B. Ps. 27281 of 1911; 1469 and 15667 of 1912; 3002, 4003, and 4004 of 1913) contain improvements in details.

A similar method is described by Harger (*J. Soc. Chem. Ind.*, 1913, p. 460).

Another instrument for the same object is that described in the French patents of Guasco, 437585, and his Ger. P. 259337. A Leslie differential thermometer is used, one bulb being coated with catalytic metal or alloy. Should inflammable gas be present in the air, its combustion, induced by the catalytic metal raises the temperature of the bulb. The thermometer stem is graduated empirically to represent certain conditions of the atmosphere. In another form of the apparatus, wires are sealed into the stem of the thermometer, and the rise of the mercury brings about a contact and rings a bell.

On the same principle is founded the apparatus of Felser (Ger. P. 266046).

An apparatus for indicating the presence of detonating gases in the air of pits, etc., is described in H. Neubaur's Fr. P. 452992; another in Philip and Steele's B. P. 5467 of 1913 and in Hobel's Ger. P. 270809.

W. Baxter (B. P. 27264 of 1912) describes an apparatus for testing gases with miners' safety lamps.

Ferrocarbonyl.

This compound occurs in slight quantities in water-gas; Roscoe and Scudder found in 1 cb.m. of such gas 2·40 g. Fe which must have been present therein in the form of FeCO. It is estimated by passing a measured volume of water-gas through a refractory glass tube, heated to red heat; it is thereby decomposed into CO and metallic iron, which is partly deposited in the tube as a dark mirror. Another portion of the iron is carried away by the gaseous current in the shape of dust, and can be retained by a cotton-wool plug, placed in the end of the tube. The iron deposited in both places is dissolved in dilute sulphuric acid and estimated by titration.

Nickel carbonyl might be estimated in a similar manner.

Nitroglycerine.

This compound may be carried into the air in the shape of fog found in blasting operations. Although its quantity will be in any case very slight, it causes even then headaches and other troubles, and its estimation may be desirable. This can be effected by agitating a measured volume of the air with alcohol which absorbs the nitroglycerin; the latter can be estimated by evaporating the alcohol at the ordinary temperature.

The analysis of nitroglycerine itself does not belong to the domain of gas-analysis; we will only mention that it is carried out by means of Lunge's nitrometer or gas-volumeter (*suprà*, pp. 21 *et seq.*).

Nitrogen Protoxide (*Nitrous Oxide*), N_2O.

This compound occurs, *e.g.*, in vitriol-chamber gases, and its estimation may be desirable in order to establish what loss of "nitre" is thereby caused in the sulphuric acid manufacture. It is pretty freely soluble in water; Bunsen expresses this solubility by the formula:

$$1{\cdot}3052 - 0{\cdot}045362t + 0{\cdot}0006843t^2.$$

Pollak, as quoted by Treadwell (*Lehrbuch*, ii. p. 565) found it

$$= 1{\cdot}13719 - 0{\cdot}042265t + 0{\cdot}000610t^2.$$

Its solubility in alcohol is even more considerable, about thrice the figure for water.

We do not as yet possess any method for the qualitative detection of small amounts of this gas. Its quantitative estimation may be performed by combustion in various ways.

Winkler (*Technical Gas-Analysis*, p. 164) proposed mixing the gas with hydrogen and passing this mixture through platinum asbestos, contained in a moderately heated tube, thus producing the reaction:

$$N_2O + H_2 = N_2 + H_2O.$$

Hence 2 vols. N_2O+2 vols. H furnish 2 vols. N_2 (the H_2O being condensed to liquid water), and the contraction produced by combustion directly indicates the volume of nitrogen protoxide. But this method is only applicable to gases containing no other constituents acting upon hydrogen, such as oxygen, nitric oxide, etc., and is therefore useless for most practical cases; certainly in the (most usual) case where the proportion of N_2O in the gaseous mixture is only very slight, especially as it involves the previous removal of the oxygen and the nitrogen acids and nitric oxide from the gas. The same must be said of the method of Bunsen, who effects the combination of nitrogen protoxide with hydrogen by explosion.

Dumreicher (*Wiener Akadem. Ber.*, 1881, p. 560) burns the gas with hydrogen in an endiometer. Hempel (*Berl. Ber.*, 1881, p. 903; *Z. Elektrochem.*, 1906, p. 200) uses the same method in his explosion pipette, employing two or three times the volume of hydrogen, and adding so much oxyhydrogen gas as will give 26 to 64 vols. of combustible gas to every 100 vols. of incombustible gas.

Knorre and Arendt (*Berl. Ber.*, 1899, p. 2136; 1900, p. 30) pass a mixture of nitrous oxide and hydrogen slowly through a red-hot Drehschmidt capillary (*vide suprà*, p. 100).

Pollak (as communicated by Treadwell, in whose laboratory the process was worked out) also tried hydrogen, but he found it preferable to employ carbon monoxide. The gas, previously freed from oxygen by passing over moist phosphorus, is mixed with carbon monoxide, and passed over platinum contained in a Drehschmidt capillary tube (p. 100). The carbon dioxide formed is determined in the usual way; its volume is equal to that of the N_2O originally present:

$$\underset{\text{2 vols.}}{N_2O} + \underset{\text{2 vols.}}{CO} = \underset{\text{2 vols.}}{CO_2} + \underset{\text{2 vols.}}{N_2}.$$

A method for estimating very small quantities of nitrogen protoxide in the exit gases from the vitriol chambers, worked out by Inglis, will be described *infrà*.

A method proposed by myself (Lunge, *Ber.*, 1881, p. 2188), founded upon the considerable solubility of nitrogen protoxide in alcohol, and decomposing the gases expelled from the latter into N and O by glowing palladium wire, is not very well adapted for the estimation of very slight percentages of N_2O.

According to Baskerville and Stevenson (*J. Ind. Eng. Chem.*, 1911, p. 579), none of the well-known methods for the determination of nitrogen protoxide in a gaseous mixture of which it is the principal constituent is quite satisfactory. Explosion with hydrogen may lead to results fully 2 per cent. below the truth, far too large an error when the object of analysis is to compare two commercial brands of compressed gas, of which few contain less than 95 per cent., and some over 99 per cent. of N_2O. Exact results may be obtained by the following indirect method: A measured volume of the gas is passed over ignited copper gauze previously reduced in a current of hydrogen, and the current of gas is followed by one of hydrogen, the water formed during this stage of the experiment being collected in a tared drying-tube. The method, of course, indicates not nitrogen protoxide alone, but also any oxygen, free and combined, contained in the gas. In practice, however, the only correction usually necessary is that for the moisture of the gas, since commercial nitrogen protoxide appears to be free from compounds of oxygen other than N_2O, and although oxygen can be detected in nearly every sample, its amount seems never to reach 0·1 per cent.

Nitric Oxide, NO.

Qualitative Detection.—This can be performed by oxidising the NO by means of atmospheric oxygen, or otherwise, whereby nitrogen peroxide is formed, and passing the gases through a dilute solution of sodium or potassium hydrate, which then contains alkaline nitrates and nitrites. The presence of the latter, and thereby the original presence of NO, is proved by acidifying the solution with acetic acid and adding the reagent of Griess, on α-naphtylamine and sulphanilic acid, as improved by Lunge. The reagent is prepared as follows: Dissolve 0·5 g. of α-naphtylamine in 20 c.c. boiling water, pour off the colourless solution from the violet residue, and add to the solution 150 c.c. of dilute acetic acid. On the other hand, dissolve 0·5 g. of sulphanilic acid in 150 c.c. of dilute acetic acid. Mix the two solutions and keep them in a tightly stoppered bottle. The reagent should be kept in the dark when not in use. For making the test heat the absorbent, which may now contain some nitrite, to about 80°, and add about one-fifth of its volume of the Griess reagent. If nitric oxide had been present in the original gas mixture, a red colour is produced. The reaction is extremely delicate, 1 part of nitrous acid in 1000 million parts of the solution producing a distinct red colour after one minute.

Quantitative Estimation of Nitric Oxide.—This has been mentioned in several previous places.

I. *By Absorbing Agents, vide* p. 128.

II. *Oxidation to Nitric Acid.*—This may be brought about by passing the gaseous mixture through absorbing bottles, or a ten-bulb absorption tube (Fig. 72, p. 146) or other efficient apparatus containing an oxidising solution. As such may be used a seminormal solution of potassium permanganate, say 30 c.c., to which 1 c.c. of sulphuric acid, specific gravity 1·8, is added. After passing a sufficient quantity of gas by means of an aspirator through this solution, the solution is titrated, preferably by adding a solution of ferrous sulphate, the relation of which to the permanganate has been ascertained, and re-titrating with permanganate till the rose colour reappears. Each cubic centimetre of permanganate consumed indicates 0·007 g. N in the shape of NO, or 0·10803 grains N per cubic foot.

Von Knorre (*Chem. Ind.*, 1902, p. 534) in the case of large quantities prefers absorbing the NO in a mixture of 5 vols. of saturated potassium bichromate solution and 1 vol. concentrated sulphuric acid, which is perfectly stable at ordinary temperatures, and does not evolve oxygen when agitated with indifferent gases, whilst oxidising the NO quantitatively to HNO_3.

Divers (*J. Chem. Soc.*, 1899, lxxv. p. 82) employs for absorbing the nitric oxide a concentrated alkaline solution of sodium or potassium sulphite, whereby hyponitrososulphate, $NaN_2O_2SO_3$, is formed. Any carbon dioxide or other acid gas present along with the nitric oxide must be previously removed by alkali.

Schönbein (*J. prakt. Chem.*, 1860, p. 265) found that nitric oxide is oxidised to nitric acid by an excess of hydrogen dioxide, and this reaction has been tried by various chemists for its quantitative estimation, *e.g.*, by myself (*Z. angew. Chem.*, 1890, p. 568), but I discarded it as not sufficiently accurate. Moser (*Z. anal. Chem.*, 1911, p. 401) states that the NO can be completely absorbed in six to twelve minutes when employing an absorption bulb designed by him (*vide infrà*).

III. *Combustion of NO by Atmospheric Air in the Presence of Potassium Hydrate.*—Baudisch and Klinger (*Berl. Ber.*, 1912, p. 3231) pass atmospheric air into the gas containing NO, standing over sticks of caustic potash in a gas-pipette. The NO is oxidised into N_2O_3 which is momentarily taken up by the KOH, so that the formation of any NO_2 is completely excluded.

The reactions are:

$$(1)\ 4NO + O_2 = 2N_2O_3.$$
$$(2)\ 4KOH + 2N_2O_3 = 4KNO_2 + 2H_2O, \text{ or:}$$
$$4NO + O_2 + 4KOH = 4KNO_2 + 2H_2O.$$

Hence 4 vols. of nitric oxide absorb 1 vol. oxygen; therefore four-fifths of the contraction observed when passing air into the pipette containing NO in contact with moistened caustic potash correspond to the NO previously present. There must be an excess of oxygen remaining at the end of the process. The sticks of caustic potash must be perfectly dry (Klinger, *Ber.*, 1913, p. 1746). The formation of NO_2 in lieu of N_2O_3 is not caused by an excess of oxygen, but by the presence of moisture.

If the NO is in excess, all the oxygen vanishes, and thus the latter can be estimated (*suprà*, p. 217).

Koehler and Marqueyrol (*Bull. Soc. Chim.*, xiii. p. 69; *J. Chem. Soc.*, civ. p. 241; *Chem. Zentralb.*, 1913, p. 957) prefer absorbing the N_2O_3 formed as above, not by potassium hydroxide, but by *monoethylaniline*, because the potassium hydroxide absorbs also several other gases (N_2O, N_2, CO_2, CO). Monoethylaniline dissolves a little more than its own volume at CO_2 at 15° to 20° under atmospheric pressure, so that when only one-sixth or one-seventh of the total pressure is due to this gas, the volume dissolved by the small amount of ethylaniline used can be neglected. They introduce 80 c.c. of the gas into a glass jar, standing in a mercury trough, together with 0·6 c.c. monoethylaniline, and by a Doyère pipette they admit oxygen bubble by bubble, so that after the absorption of all the NO about 5 c.c. remain behind. The gas is then separated from the liquid, measured, and the CO_2 absorbed by 0·2 c.c. standard alkali solution, after which the gas is again measured.

To test whether all the nitric oxide has been absorbed by one of oxidising agents employed, Lunge and Ilosvay (*Z. angew. Chem.*, 1890, p. 568) employ the reagent of Griess as modified by Lunge (*vide suprà*, p. 316) by allowing the air to mix with the gases as they leave the bulb-tube, and then examining for higher oxides of nitrogen. The above reagent will always show a slight reddening with such gases, even where the absorption has been made as complete as possible; but for most practical purposes such traces may be neglected.

IV. *Reaction of Nitric Oxide with Hydrogen.*—Knorre and Arendt (*Ber.*, 1899, p. 2136) mix the gas with hydrogen and pass the mixture *very slowly* through a Drehschmidt's platinum capillary (p. 100), heated to a bright red heat. Under these circumstances the combustion takes place according to the following equation:

$$\underset{4\text{ vols.}}{2NO} + \underset{4\text{ vols.}}{2H_2} = \underset{0\text{ vol.}}{2H_2O} + \underset{2\text{ vols.}}{N_2}.$$

Hence each volume of nitric oxide present corresponds to a contraction of $1\frac{1}{2}$ volumes, or two-thirds of the contraction = NO. If the gas is passed too quickly or the heating of the capillary is insufficient, some ammonia is formed, producing wrong results.

Nitric oxide cannot be burned by explosion with hydrogen; if, however, much nitrogen protoxide is present, there is a violent explosion, but no quantitative combustion of the nitric oxide.

V. *Reaction of Nitric Oxide with Carbon Monoxide.*—L. Pollak (as quoted by Treadwell, vol. ii. p. 567) found that a mixture of NO and CO can be burnt by passing it through a Drehschmidt's platinum capillary, if at the same time the carbon dioxide formed is removed. This is done by placing on the mercury in the pipette connected with the Drehschmidt capillary a few cubic centimetres of caustic potash solution, which absorbs the CO_2 as it is formed. If this is neglected, the combustion is not quantitative.

The reaction is:

$$\underset{4\text{ vols.}}{2NO} + \underset{4\text{ vols.}}{2CO} = \underset{0\text{ vol.}}{2CO_2} + \underset{2\text{ vols.}}{N_2},$$

corresponding to a contraction $= \frac{3}{2}$ of the volume of NO.

If at the same time much nitrogen protoxide is present, the combustion of the NO in the Drehschmidt capillary is quantitative, even without absorbing the CO_2 formed:

$$\underset{4\text{ vols.}}{2NO} + \underset{4\text{ vols.}}{2CO} = \underset{4\text{ vols.}}{CO_2} + \underset{2\text{ vols.}}{N_2}.$$

Here the contraction is $= \frac{1}{2}$ vol. of the nitric oxide.

Analysis of Gas Mixtures containing both Nitrogen Protoxide and Nitric Oxide (Moser, *Z. anal. Chem.*, 1911, l. p. 401).—The separation of N_2O and NO cannot be effected by dissolving out the NO by means of a solution of ferrous sulphate, for the N_2O is soluble to some extent in water, even when this is saturated with a salt such as ferrous sulphate. Previous saturation of the ferrous sulphate solution with nitrous oxide changes the large positive error to a small, but not insignificant negative one, for the absorption of NO by the liquid reduces its capacity to hold N_2O in solution, and this gas is set free. The method proposed by Divers (*Trans. Chem. Soc.*, 1889, p. 82; *vide suprà*, p. 317) viz., absorption of the NO by sodium sulphite solution, gives no better results. The gravimetric methods for the estimation of NO are very troublesome and rarely applicable. The volumetric method of oxidising the NO by permanganate, which has no action on N_2O, for which Lunge (*Z. angew. Chem.*, 1890, p. 568) has designed a special apparatus (the ten-bulb tube, p. 146), may also lead indirectly to errors, owing to the necessity of displacing the air by CO_2. This is avoided by Moser, by passing the gas to be analysed into an absorption vessel previously filled with standardised potassium permanganate solution; after shaking well to complete the reaction, the diminution in the strength of the permanganate is measured. Or else the apparatus is filled with hydrogen peroxide solution, and the nitric acid formed from the NO determined by titration with standard alkali. Of course here the presence of acid vapours must be avoided.

The following method for estimating both NO and N_2O has been proposed by Knorre (*loc. cit.*):—The gas is mixed with an excess of *hydrogen* and burnt in a bright red-hot Drehschmidt capillary. If we call the volume of $N_2O = x$, that of $NO = y$, we have:

$$\begin{array}{ccc} N_2O & & NO \\ x & + & y = V \\ x & + & \frac{3}{2}y = V_c \text{ (contraction)}, \end{array}$$

from which we find:

$$x = 3V - 2V_c$$
$$y = 2(V_c - V).$$

Or else the gaseous mixture is mixed with an excess of *carbon monoxide*, burnt in the bright red-hot Drehschmidt capillary, and the contraction (V_c) and the CO_2 formed (V_k) are measured:

$$\begin{array}{cc} N_2O & NO \\ \multicolumn{2}{c}{x + y = V_k} \\ \multicolumn{2}{c}{\frac{1}{2}y = V_c} \end{array}$$

therefore:

$$x = V_k - 2V_c$$
$$y = 2V_c.$$

Moser (*loc. cit.*) objects to the estimation of N_2O by burning a mixture of it with hydrogen that ammonia is formed as a by-product, and that platinum is permeable to gases at a red heat.

The method of Baudisch and Klinger (p. 318), viz., oxidation of the NO to N_2O_3, may also be used in the presence of N_2O.

Estimation of Nitrogen Protoxide, Nitric Oxide, and Free Nitrogen in Presence of One Another.—According to Knorre, either by burning with *hydrogen* or with *carbon monoxide* in the Drehschmidt capillary. In the case of hydrogen, we note the contraction (V_c), add to the gaseous remainder an excess of oxygen, and burn in the capillary. Two-thirds of the ensuing contraction is equal to the hydrogen not consumed in the first combustion; this magnitude, deducted from the hydrogen originally used, indicates the hydrogen consumed (V_w).

Now we have:

$$\begin{array}{l}
\quad N_2O \quad NO \quad N \\
x + y + z = V \\
x + \frac{2}{3}y = V \\
x + y = V_w
\end{array}$$

from which we find:

$$\begin{aligned}
x &= 3V_w - 2V_c \\
y &= 2(V_c - V_w) \\
z &= V - V_w.
\end{aligned}$$

If we burn the gases with carbon monoxide, we have:

$$\begin{array}{l}
\quad N_2O \quad NO \quad N \\
x + y + z = V \\
\frac{1}{2}y = V_c \text{ (contraction).} \\
x + y = V_k \text{ (carbon dioxide),}
\end{array}$$

from which we find:

$$\begin{aligned}
x &= V_k - 2V_c \\
y &= 2V_c \\
z &= V - V_k.
\end{aligned}$$

In gaseous mixtures containing, besides N_2O, NO, and N, also *carbon dioxide*, this must be first absorbed by the smallest possible quantity of highly concentrated caustic potash solution, whereupon the analysis of the gaseous remainder is performed as just described.

Nitrogen Trioxide and Peroxide.

Reich's method (*suprà*, p. 137) has been also applied to the estimation of the active nitrogen acid equivalent to nitrogen trioxide, N_2O_3, in the gases of vitriol-chambers and Gay-Lussac towers, etc. The absorbent is a decinormal solution of potassium permanganate, mixed with about the same volume of dilute sulphuric acid. The end of the reaction is indicated by the liquid being decolorised, but the absorption takes place slowly and somewhat incompletely. We must, moreover, consider that the atmosphere of the vitriol-chambers does not contain the active nitrogen oxides in the shape of N_2O_3, as formerly assumed, but that the nitrogen trioxide is almost entirely dissociated into nitric oxide and nitric peroxide, mostly together with an excess of either one or the other of these oxides. By the method just described we learn how much of the exact mixture of $NO+NO_2 \rightleftarrows N_2O_3$ is present. But as in most cases the chamber-gases contain an excess of either NO or NO_2 above that proportion, the operation of determining by Reich's or any other method the amount of oxygen required for forming nitric acid is quite inaccurate. This also holds good of the modification, consisting in passing a certain volume of the chamber-gases through concentrated sulphuric acid, which certainly retains the mixture of $NO+NO_2$ in the shape of nitrososulphuric acid, but also any NO_2 present in excess, in the shape of nitrososulphuric acid and nitric acid; the latter would not be indicated when titrating the solution with potassium permanganate. If, on the contrary, NO is in excess, this would be lost. That solution of nitrogen oxides in concentrated sulphuric acid should not be tested by the permanganate method (by which any NO_3H formed from NO_2 would be lost), but by the nitrometer to be described. In the back chambers there is an excess of NO_2 in the gases, and here the mixture of nitrogen oxides can be directly absorbed in concentrated sulphuric acid, and then tested in the nitrometer. In the front chamber there is an excess of NO, and here the gases, after absorption by concentrated sulphuric acid, should be oxidised by permanganate as described *suprà*, p. 317, and the solution obtained again tested in the nitrometer.

Estimation of Nitrous Fumes produced by Explosion.—Heymann (*J. Soc. Chem. Ind.*, 1913, xxxii. p. 674) estimates the nitrous fumes, produced especially by the explosion of "cheesa" sticks, by means of a bottle containing at the bottom a solution of sodium hydroxide, through the cork of which pass three copper wires, one of them for carrying a small porcelain crucible containing the substance to be treated; the other two wires, dipping into the crucible, are connected by a thin platinum wire, and outside the bottle with a storage battery, so that the substance can be ignited by turning on the current. The fumes evolved are absorbed by the caustic soda solution, and ultimately the nitrogen oxides contained therein are reduced by zinc, the ammonia evolved indicating the amount of nitrogen oxides.

Free Nitrogen.

Nitrogen can be completely oxidised to nitric acid by mixing it with oxygen and treating the mixture with strong electric sparks. According to Hempel (*Gasanal. Methoden*, 4th ed., p. 148), it is absorbed by a red-hot mixture of 1 g. magnesium, 5 g. freshly ignited lime, and 0·25 g. sodium. But these methods are only used for isolating the helium, etc., accompanying it in atmospheric air, in gases from mineral springs, etc., which are not oxidised or absorbed by these methods.

In the ordinary way of technical gas-analysis, the nitrogen is only estimated by difference, after estimating all other gaseous constituents present.

Nitrogen, according to Bunsen, is not burnt when exploding fulminating gas in presence of air, if no more than 30 vols. of combustible gas is present to 100 vols. of incombustible gas. When burning gases containing nitrogen by the Drehschmidt platinum capillary, no nitrogen is oxidised.

Ferry's apparatus for the volumetric estimation of nitrogen (sold by Greiner and Friedrichs, Stützerbach, *Chem. Zeit. Rep.*, 1912, p. 349) contains a cylinder where CO_2 is retained by caustic potash solution, with a spiral for the better contact of the gas with the solution; on the top of the cylinder there is a glass tap, surmounted by a dish where the nitrogen, now free from CO_2, is carried into a measuring-tube, employing another confining liquid.

The apparatus of Henrich and Eichhorn for removing free nitrogen from gaseous mixtures by burning with oxygen through the action of electric sparks has been mentioned *suprà*, p. 172.

Natus (*Z. anal. Chem.*, 1913, pp. 265 *et seq.*) effects the direct determination of elementary nitrogen in gaseous mixtures with the help of calcium carbide (already recommended by Franz Fischer and Ringe in *Ber.*, 1908, p. 2017). He absorbs it by contact with a finely powdered mixture of commercial calcium carbide with one-tenth of its weight of fused calcium chloride at 900° to 1000°. The product (calcium cyanamide) is then treated by Wilfarth's modification of Kjeldahl's method (in which the substance is heated with a mixture of concentrated and fuming sulphuric acids and a drop of mercury). A known weight of the carbide mixture (previously heated in a current of hydrogen to remove volatile impurities) is introduced into a porcelain boat within a porcelain tube which is connected at either end with gas-burettes; the apparatus is filled with pure, dry hydrogen, and then the carbide is heated, and the gas to be absorbed is introduced, the absorption being completed by slowly passing the gaseous residue twice backwards and forwards through the tube. The absorption product, after cooling, is transferred to the decomposition flask and at once moistened with sulphuric acid (not water); decomposition is complete in about an hour with Wilfarth's mixture, and the cool diluted liquid is rendered alkaline, treated quickly with potassium sulphate solution, and distilled in the presence of zinc dust. The average loss of nitrogen in the process (with water in the gas-burettes) is 1·9 per cent. (maximum 3·6), or, with dry gas contained over mercury, 0·75 per cent. (maximum 1·4).

Ammonia.

The estimation of ammonia in technical gas-analysis takes place in the manufacture of illuminating gas, from which it must be completely removed, both for its use for lighting and for heating purposes, apart from its utilisation as a valuable by-product of the gas manufacture.

Its estimation in the *crude* gas has the object of ascertaining the yield of NH_3 from the coal carbonised, but more particularly of checking the work of the scrubbers or other apparatus applied for removing it from the gas. Thus, for instance, the gas from the retorts may per 100 cb.m. contain 412 g., in front of the scrubbers 375 g., behind the scrubbers 0·9 g., behind the oxide of iron purifiers merely a trace of NH_3.

In normal working like this, the removal of the ammonia from the gas is practically complete, but in case of disturbances, *e.g.*, when overtasking the apparatus by a sudden increase of the production of gas, or by insufficient cooling, or mistakes made in the working of the scrubbers, etc., on the other hand, 10 or up to 20 per cent. of the ammonia may remain in the gas.

In properly purified street-gas there are only slight traces of ammonia, hardly ever more than 0·5 g. per 100 cb.m. In England 0·5 to 2·0 grains NH_3 per 100 cb. ft. is the maximum allowed.

Still, an occasional control of this should be made, for even such slight quantities of ammonia may do damage, *e.g.*, by the formation of cyanogen hydride in gas burning with a smoky flame, by the formation of traces of nitric oxide and nitrogen trioxide, by acting on the metal of the gas-meters, etc.

The estimation of ammonia, both in the crude and in the purified gas, takes place by absorption and titration with standard acid; normal or seminormal acid being used for crude gas, decinormal acid for street-gas. The best indicator is an aqueous solution of methyl orange (1 : 1000 water), or an alcoholic solution of dimethyl-amidoazobenzene (1 : 200). When testing crude gas containing much tar, which imparts a brown colour to the absorbing liquid, fluorescein is preferable; it indicates the neutralisation of the acid by the cessation of the fluorescence, which is best observed when placing the glass on glazed black paper. Both these indicators are not affected by carbon dioxide or hydrogen sulphide, whilst rosolic acid is not quite unaffected by them.

The absorption of the ammonia by the standard acid is carried out in one of the numerous apparatus constructed for such purposes, many of which have been described in previous chapters, *e.g.*, pp. 65, 71, 76, 84, 102, 106, 145, 146, 147. Care must be taken that the glass of which they are made has not by itself an alkaline reaction, and that a minimum of rubber tubing is used for making the connections. In the case of unscrubbed gas the sample should always be taken by means of a tube projecting into the main, as the inner surface of the latter is always coated with tar. Even when using all precautions, exact results are sometimes difficult to obtain on account of the tar-fog present in crude gas, which makes the end-point of the titration more difficult to observe. If this tar-fog is removed by a cotton-wool filter, as described on pp. 307 *et seq.*, the results are too low, because the filters also remove some of the ammonia from the gases. On the whole, it is best not to attempt removing the tar-fog, and to allow for the fact that the tendency is then for the results to be rather too high. In case of necessity the ammonia may be estimated in the ammonium sulphate obtained by Knop's well-known azotometer.

When testing crude gas containing very much ammonia, the quantity of gas required for a test is correspondingly small, and this is often conveniently measured by a graduated aspirator instead of a meter. This is even necessary where the gas to be tested is under a pressure less than that of the atmosphere, in which case the aspirator draws the gas from the main through the absorbing apparatus. Where a meter is used, and the gas contains sulphuretted hydrogen, a small oxide of iron purifier should be placed between the absorbing apparatus and the meter, as otherwise the metal of the latter would be rapidly corroded.

The determination of ammonia in illuminating gas is treated in a technologic paper No. 34, of the U.S. Bureau of Standards.

For testing street-gas, S. Elster, of Berlin, sells a gas-meter which after the passage of 100 litres automatically interrupts the further passage.

In Pfeiffer's method for estimating the naphthalene vapour in gas, described *suprà*, p. 300, the ammonia contained in the gas must be completely retained by an acid washing, and this may be used for estimating its quantity at the same time.

L. W. Winkler (*Z. angew. Chem.*, 1913, p. 231) absorbs the ammonia by a solution of boric acid and titrates it by standard acid, employing congo-red or methyl orange as indicator.

The *estimation of pyridine* in the presence of ammonia is effected by Bayer (*J. Gasbeleucht.*, 1912, p. 513) by precipitating the ammonia in the shape of ammonia-magnesia phosphate, filtering, distilling the filtrate and titrating the distillate, ferrirhodanide serving as indicator.

Baessler (*J. Gasbeleucht.*, 1912, p. 905) distils solutions containing both ammonia and pyridine, with an excess of caustic soda, decomposes the ammonia contained in the distillate by sodium hypobromite solution, and distils the pyridine remaining behind into standard sulphuric acid.

Cyanogen and Hydrogen Cyanide.

About 2 or 3 per cent. of the nitrogen of the coal is in its dry distillation converted into cyanogen and its compounds. A small portion of this is retained in the hydraulic main, the coolers and scrubbers, much more of it in the oxide of iron purifiers, but some of the cyanogen always remains in the street-gas. The cyanogen compounds retained in the purifiers impart a much greater value to the spent oxide than it would otherwise possess, wherefore their estimation in the crude gas and the purified gas is of economical importance. Drehschmidt (*J. Gasbeleucht.*, 1892, p. 268) calculated that already at that time the cyanogen remaining in the street-gas of Berlin represented a value of £2150 per annum.

In a special instance, Leybold (*J. Gasbeleucht.*, 1890, p. 366) found in 100 cb.m. gas the following quantities of cyanogen or its compounds:—

In the hydraulic main	256·1 g.	
After cooling	246·5 "	
" scrubbing	242·4 "	
" the first oxide purifier	126·8 "	
" the second "	80·2 "	
" the third "	59·3 "	
In the gas-holder	39·7 "	
Removed by cooling	3·76 per cent.	
" scrubbing	1·62 "	
" oxide (1)	45·09 "	71·45 per cent.
" " (2)	18·12 "	
" " (3)	8·16 "	
Remaining in the street-gas	15·50 "	

The hydrogen cyanide present in street-gas must strongly increase its poisonous properties, whilst free cyanogen (dicyanogen) is not poisonous. Unfortunately no analytical methods exist for the quantitative separation of HCN and $NC \equiv CN$. Both of them, however, quickly destroy the iron parts of the gasholders and the metal of the meters, unless these are specially protected.

The *qualitative detection* of cyanogen, either free or in the state of HCN, is effected according to Kunz-Krause (*Z. angew. Chem.*, 1901, p. 652), who bases himself on a reaction indicated by Schönbein and Pagenstecher, by filtering paper, soaked successively in a solution of cupric sulphate (1 : 1000) and freshly prepared tincture of guaiac resin (3 per cent.), which is thereby coloured blue. This extremely sensitive reaction can do very good service in the detection of very slight escapes of coal-gas. Schaer has made it even more sensitive by using guaiaconic acid in place of the gum guaiac. Brünnich (*Chem. News*, cxxxvii. p. 173) moistens the test paper with formalin before exposing it to the gas mixture.

The *quantitative estimation* of the total cyanogen contained in the crude or purified gas is mostly effected by a process first indicated by Gasch (*J. Gasbeleucht.*, 1890, p. 215) which we describe in the form given to it by Drehschmidt (*loc. cit.*). Both free cyanogen and hydrocyanic acid are retained, even in the presence of CO_2 and H_2S, by a solution of potassium hydroxide, containing freshly precipitated ferrous hydrate, with formation of ferrocyanide. For each test 100 litres of gas, at the rate of 60 litres per hour, is passed through two bottles of the shape shown in Fig. 124, where the entrance pipe ends at the bottom of the bottle in a perforated bulb. The first bottle is charged with 15 c.c. of a solution of ferrous sulphate (1 : 10) and 15 c.c. of a solution of commercial caustic potash (1 : 3); the second with 5 c.c. of ferrous sulphate solution, 5 c.c. caustic potash solution, and 20 c.c. water. Behind these comes the gas-meter. At the end of the test the contents of both bottles are washed out, made up to 250 c.c., and poured on to a dry filter. Two hundred c.c. of the clear filtrate = 80 litres gas is neutralised with sulphuric acid; add 2 g. ammonium sulphate, 15 g. mercuric oxide (to remove H_2S), and a few drops of liquor ammoniæ, heat to boiling, and continue this gently for a quarter of an hour. After cooling dilute to 300 c.c. and filter again through a dry filter. Of the clear liquor thus obtained, pour 250 c.c., corresponding to 66·66 litres of gas, into a 300 c.c. flask, add 6 or 8 c.c. of liquor ammoniæ sp. gr. 0·91, and 7 g. zinc dust, shake well up, add 2 c.c. caustic-potash solution (1 : 3), fill up to the mark, shake up again, and filter through a double filter. Titrate 200 c.c. of the fitrate = 44·44 litres gas, by adding 10 c.c. deci-

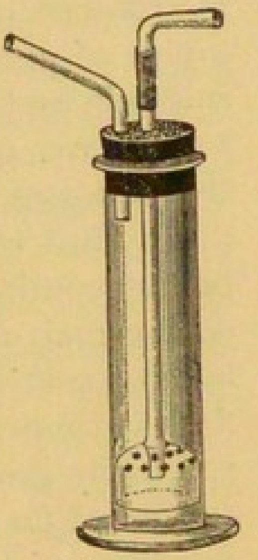

FIG. 124.

normal silver solution, acidulating with nitric acid, and remeasuring the excess of silver by decinormal ammonium sulphocyanide solution and iron alum as indicator. Each cubic centimetre $\frac{1}{10}$ normal silver nitrate consumed = 0·002584 g. cyanogen.

The ferrocyanide contained in the absorbing bottles can also be estimated by the method of Feld (*J. Gasbeleucht.*, 1903, p. 561), which is founded upon a method proposed by Rose and Finkener (*Z. anal. Chem.*, 1862, p. 299). It is founded on the fact that mercuric oxide converts a boiling solution of a soluble ferrocyanide into mercuric cyanide, from which the hydrocyanic acid may then be recovered by distillation with sulphuric acid in presence of chlorides. A solution containing about 0·3 to 0·5 g. of potassium ferrocyanide or its equivalent, freed from sulphide by lead carbonate, if necessary, is diluted to about 150 c.c., 10 c.c. of normal sodium hydroxide solution added, and the mixture heated to boiling. Then 15 c.c. of trinormal magnesium chloride solution is added in a thin stream, and the boiling continued for five minutes. One hundred c.c. of boiling decinormal mercuric chloride solution are then added, and the boiling continued for a further ten minutes, after which the flask is connected to a condenser, 30 c.c. of 4 N-sulphuric acid run in by means of a stoppered funnel, and the distillation is continued for twenty to thirty minutes, the end of the condenser dipping under the surface of 25 c.c. of normal sodium hydroxide solution, placed in the receiver. Thereby the HCN present as ferrocyanide is obtained in the receiver as a solution of sodium cyanide, the amount of which is determined by dilution to 300 to 400 c.c., adding a little potassium iodide and titrating with decinormal silver nitrate until a permanent yellow precipitate of AgI is formed. Each cubic centimetre of $N/10$ silver nitrate solution indicates 0·0052 g. $NC{\equiv}CN$, 0·005403 g. HCN, 0·01409 g. $K_4 Fe (CN)_6 . 3H_2O$, or 0·00956 of $Fe_7 (CN)_{18}$.

Many analysts have approved of this method. Skirrow (*J. Soc. Chem. Ind.*, 1910, p. 319) obtained with it low results, but Colmann (*Analyst*, 1910, p. 295) states the results to be substantially accurate. Pfeiffer (Lunge-Berl's *Unt. Meth.*, iii. p. 343) approves of it as well.

Detection and Determination of Cyanogen in Presence of Hydrogen Cyanide.—Rhodes (*J. Ind. and Eng. Chem.*, 1912, iv.

p. 652), basing upon an observation made by Wallis (Liebig's *Ann.*, 1906, cccxlv. p. 353), proceeds as follows:—Test-tubes 15 c.m. long and provided with side arms are used for absorbing the gases. In one such tube is placed 10 c.c. of a 10 per cent. solution of silver nitrate to which 1 drop of $\frac{1}{6}$ normal nitric has been added. In the second tube is placed 10 c.c. of a twice-normal solution of potassium hydroxide. The two absorption tubes are connected in series and the gas mixture is passed through. Since the first tube is intended to hold back the hydrogen cyanide, the passage of the gas must be stopped before all the silver nitrate in this tube has been converted into cyanide. After the gas mixture has been passed through for a sufficient length of time, a current of air is passed through for ten minutes. The second tube, which contains the potassium hydrate solution, is then disconnected, and 5 c.c. of a solution of ferrous sulphate and 1 drop of a solution of ferric chloride are added to its contents; after about fifteen minutes dilute sulphuric acid is added, to dissolve the ferrous and ferric hydroxide. The appearance of a blue-green colour after acidification proves the presence of cyanogen in the original gas mixture. As small an amount of cyanogen as 0·3 c.c. may be detected in this manner, even in the presence of 10 c.c. of hydrogen cyanide, and even when 20 litres of air was passed through the apparatus subsequent to the introduction of the cyanogen. Carbon dioxide interferes only if sufficient of it is present to convert all the KOH into K_2CO_3. The presence of hydrogen cyanide in the original gas mixture is detected by collecting on a filter any precipitate formed in the first absorption tube which contains the silver nitrate, washing it with very dilute nitric acid, drying it, transferring it to a small sublimation tube, and warming it with about 5 mg. of iodine. The formation of a sublimate of cyanogen iodide on the side of the tube proves the presence of silver cyanide in the precipitate; 0·1 mg. of silver cyanide, equivalent to 0·02 mg. of hydrogen cyanide, may be detected in this manner.

To determine cyanogen and hydrogen cyanide in the presence of each other, the gas mixture is passed through a series of four absorption tubes. Each of the first two of these tubes contains 5 c.c. of a standardised decinormal solution of silver nitrate and 1 drop of dilute nitric acid; the third tube contains 10 c.c. of a twice-normal solution of potassium hydroxide, free from chloride, and the fourth tube 5 c.c. of this solution. The gas to be examined is slowly passed through, or is carried through by a slow current of air. The contents of the first two absorption tubes are placed on a filter, and the soluble silver salts washed out with very dilute nitric acid. The filtrate and washings are titrated with a standardised solution of ammonium sulphocyanate, ammonium ferric alum serving as indicator, which shows the hydrogen cyanide present in the original gas mixture. The contents of the third and fourth absorption tubes are placed in a beaker, an excess of a standard silver nitrate solution is added, constantly stirring, and then dilute nitric acid, until the silver oxide has redissolved and the solution is slightly acid. The precipitate of silver cyanide is filtered off, the soluble silver salts washed out with very dilute acid, and the filtrate and washings titrated with ammonium sulphocyanide, ammonium-ferric alum serving as indicator. From this the cyanogen present in the original gas mixture is calculated, the reactions being:—

$$\begin{aligned}(CN)_2 + 2KOH &= KCN + KCNO + H_2O,\\ KCN + AgNO_3 &= AgCN + KNO_3,\\ AgNO_3 + KCNS &= AgCNS + KNO_3.\end{aligned}$$

Detection of Hydrogen Cyanide.—We have spoken of this already *suprà*, p. 328. Another test for it is the formation of Prussian blue, when passing the gas through a solution of potassium hydroxide, adding ferrous sulphate and 1 drop of ferric chloride, gently warming and acidifying with hydrochloric acid. Free cyanogen will equally produce this reaction.

Or else add ammonium sulphide in excess, then ammonia or a drop of caustic soda solution, and heat until the excess of ammonium sulphide has been driven off and the solution is again colourless. The solution will then contain sulphocyanate, which after acidification gives a blood-red colour with ferric chloride.

Quantitative Determination of Hydrogen Cyanide.—According to L. W. Andrews (*Amer. Chem. J.*, 1903, xxx. p. 187) the gas is absorbed in potassium hydroxide solution, which is diluted until it contains no more than 1 per cent. of HCN. Now 2 drops of a solution of paranitrophenol are added. If thereby a yellow colour is produced, decinormal hydrochloric acid is added until the colour has nearly disappeared. On the other hand, if the solution remains colourless, decinormal caustic potash solution is added until a very pale yellow tint is observed. Now add 15 to 20 c.c. of a solution of 40 g. of mercuric chloride in a litre, stir the solution and allow it to stand for one hour at the temperature of the air. The HCl set free by the reaction: $HgCl_2 + 2HCN = Hg(CN)_2 + 2HCl$, is then titrated with a decinormal solution of potassium hydrate, the end-point being shown by the appearance of a pale yellow tint in the solution.

Hydrogen Chloride.

This gas is but rarely looked for in technical gases, with two certainly most important exceptions, viz., first, the exit-gases from the ordinary hydrochloric acid (muriatic acid) condensers, employed in the saltcake manufacture by the ordinary process, and secondly, in the gases produced in the Hargreaves process.

1. *Exit-gases from the Condensers in the Manufacture of Sulphate of Soda from Common Salt in Decomposing Pans.*—According to the British Alkali Act of 1906, 95 per cent. of all the hydrochloric acid produced in a works must be condensed, and no gases are permitted to escape into the atmosphere which contain more than $\frac{1}{5}$ grain HCl per cubic foot (=0·457 g. per cubic metre). The total acidity of all the gases present must not exceed the equivalent of 4 grains SO_3 per cubic foot (=9·15 g. per cubic metre). The volume of the gases is understood as reduced to 60° F. (15·5° C.) and 30 ins. mercury (almost exactly 760 mm.).

The examination of the chimney-gases is carried out by the inspectors by means of a Fletcher bellows, as described in Lunge's *Sulphuric Acid and Alkali*, 4th ed. 1913, i. p. 768, which serves both as aspirator and absorbing vessel; but of course any other of the various absorbing apparatus described in this treatise may be used for this purpose. The Fletcher bellows are constructed to draw $\frac{1}{10}$ of a cubic foot of gas at one aspiration, but they should in all cases be standardised by filling with air at the normal working capacity, and measuring the volume aspirated by expelling it into an inverted graduated vessel filled with water, correcting the volume obtained for temperature and pressure. In examining chimney-gases or other gases, the bellows are connected with the chimney by means of a porcelain, glass, or platinum tube of 12 mm. diameter, which extends some considerable distance into the chimney. Both bellows and tube are first washed out with distilled water, 200 to 300 c.c. of distilled water then introduced, and the necessary number of aspirations made. The contents of the bellows are well shaken after each aspiration to allow all the acids present to be dissolved by the water. When the operation is complete, a little water is forced into the connecting tube and allowed to flow back into the bellows in order to wash out any acid that may have condensed in the tube. The liquid in the bellows is then washed into a porcelain dish, and, if necessary, filtered from soot. Any sulphurous acid present is oxidised by potassium permanganate, excess of the latter removed by a trace of ferrous sulphate, the solution neutralised by pure sodium carbonate, a little potassium chromate added, and the whole titrated with decinormal or centinormal silver nitrate solution. Each 1 c.c. decinormal silver nitrate solution $=0{\cdot}003647$ g. HCl.

In the *Alkali Inspectors' Report* for 1898, pp. 11 *et seq.*, an addition of hydrogen peroxide, free from chlorine, to the water put into the bellows was recommended, to effect the immediate oxidation of any sulphur dioxide present in the gases. The total acidity is determined by titration with sodium carbonate solution, and subsequently the chlorine by means of standard silver nitrate solution. Certain difficulties are liable to occur when working in this manner. Thus discoloration may arise owing to incomplete oxidation of organic matter by the hydrogen peroxide, and this may under certain conditions lead to the reduction of the chromate; further, it is difficult to obtain hydrogen peroxide free from chlorine. For these reasons the process has been modified, and is now carried out as follows:—The total acidity is determined as before with sodium carbonate solution and methyl orange, a few drops of potassium permanganate being added where the solution is very dark owing to the presence of sooty matter. The neutralised solution is treated with 0·5 g. of calcium or magnesium carbonate, followed by 5 to 10 drops of a 5 per cent. ferrous sulphate solution, the mixture stirred for a minute, and then decanted or filtered. The chloride is then estimated in the filtrate in the usual manner. The addition of ferrous sulphate gets rid of the organic matter which is carried down with the ferrous carbonate precipitate, and so gives a neutral solution in which the hydrogen peroxide will not exert any reducing action on the chromate; also, it precipitates the arsenic and copper present in the gases from copper works. The potassium permanganate, added to oxidise the organic matter, must be employed with caution, since the manganese sulphate produced may reduce the chromate, with production of a green coloured solution; this will, however, not occur if the solutions are neutralised as described.

Should any of the difficulties above referred to be met with, it is best to oxidise with nitric acid and estimate the chloride by Volhard's method (employing ammonium thiocyanate for titration).

A continuous test may of course be made, as in the case of the exit-gases of the sulphuric acid process (*infrà*, p. 337), by employing a large aspirator and selecting a suitable type of absorption apparatus.

2. *Gases evolved in the Hargreaves Process.*—By this process, sodium chloride contained in large iron cylinders is directly converted into sulphate by drawing the gases from pyrites kilns, together with steam, through the salt, whereby the sulphur dioxide of the gases is gradually absorbed and in its place hydrogen chloride is liberated. The progress of the reaction must be constantly followed by taking samples of the gases passing through the connecting pipes between the cylinders, and testing these as follows:—

(*a*) For *total acidity*, preferably by the method of Lunge (p. 141).

(*b*) For *sulphur dioxide*, by the method of Reich (pp. 137, 243).

(*c*) For *hydrogen chloride*. This is found by titrating the sample, taken for test (*a*) with silver nitrate, either by the ordinary method of Mohr and others, or by Volhard's method.

The content of *sulphur trioxide* is obtained by deducting $b + c$ from a.

In the daily practice it is sufficient to apply either a or b, but in every case the test (c) must be made.

A method for *detecting and estimating hydrogen chloride, bromide, or iodine in the presence of hydrogen cyanide* is described by Polstorff and Meyer (*Z. anal. Chem.*, 1912, li. p. 601). A portion of the solution, which must not be too concentrated, is cooled down, rendered alkaline, and formic aldehyde added, with agitation, until the smell is strongly felt. If now nitric acid is added, the presence of halogenides is found on addition of silver nitrate. For their quantitative estimation, first the cyanogen contents are ascertained by Liebig's method; then about 0·6 of the substance is dissolved in 100 c.c. water, the solution rendered alkaline, 20 or 30 drops of 35 per cent. formic aldehyde solution added, after a few minutes acidulated with nitric acid, and the halogen contents estimated by Volhard's method.

EXAMINATION OF GASES IN THE MANUFACTURE OF SULPHURIC ACID BY THE LEAD-CHAMBER PROCESS.

We must distinguish the following three cases:—

1. *Gases before entering into the Chambers.*—This extends merely to their content of sulphur dioxide, sometimes also of sulphur trioxide; and is mostly carried out by the method of Reich, as modified by Lunge (*suprà*, p. 141). *Cf.* also the methods described, pp. 243 *et seq.*

2. *Gases of the Lead Chambers* (*Vitriol Chambers*).—These are generally only examined by observing the colour (more particularly in the back-chambers and in getting out), the temperature, and the pressure under which they stand. A chemical analysis of these gases is generally not made, and under ordinary working conditions but little advantage would be derived from it, owing to the difficulty of obtaining really average samples; moreover, it is unnecessary since the process is controlled by analysing the inlet- and exit-gases (Nos. 1 and 3). If exceptionally such an analysis has to be made, it can be carried by the methods described *infrà* for the investigation of the exit-gases. For more exact determinations, which do not enter into the ordinary sphere of technical gas-analysis, we refer to the

methods employed by Lunge and Naef (*Chem. Ind.*, 1884, pp. 5 *et seq.*) and Trautz (*Z. physik. Chem.*, 1904, p. 526). We also refer to the method of Raschig for the estimation of these gases for sulphur dioxide and nitrous compounds (*suprà*, p. 244).

3. *Exit-gases from the Gay-Lussac Towers*—(a) Estimation of *free oxygen.*—This is the most important factor for regulating the working of the chambers in general, and the damper in the outlet pipe in particular.

The oxygen is estimated by absorbing it, and measuring the resulting decrease in volume. The various methods employed for this purpose have been described in detail *suprà*, pp. 119 and 211. We especially recommend the employment of moist phosphorus in very thin sticks, which is much less troublesome and expensive than that of pyrogallol. It must, however, be remembered that phosphorus is not acted upon by oxygen at temperatures below 15°; therefore, if the apparatus is standing in a cold place, the absorption vessel must be slightly warmed. Since the water with which the phosphorus is moistened would also absorb the acids contained in the gas, this must be passed through caustic potash solution before absorbing the oxygen.

Where, as usual, only several tests are made in the course of the day, the use of a special aspirator is unnecessary; the gas-burette itself may be used as such by filling and emptying it three or four times in succession from the opening in the gas main provided for taking samples. It is, however, advisable to make a *continuous* test, in addition to the above, by drawing the gas slowly during the full twenty-four hours into a vessel from which the sample for analysis is taken. For this purpose an aspirator of wood or metal may be employed, if the acid vapours are previously removed from the gases, which is suitably done in connection with the absorbing apparatus. On the other hand, more simple apparatus may be used, provided they permit at least 10 litres of the gas to be passed through and measured during the twenty-four hours, in order to obtain a really representative average sample.

The estimation of oxygen by means of moist phosphorus is conveniently carried out in an Orsat apparatus, pp. 66 *et seq.*, with two absorbing vessels, one of which is charged with caustic potash solution for the absorption of acids, the other with very thin sticks of moistened phosphorus. The manipulation is described *eodem loco*. A very convenient form of apparatus, devised by Strype for the analysis of exit-gases, is described in Lunge's *Sulphuric Acid and Alkali*, 3rd ed., i. p. 739. Other apparatus have been described, *e.g.*, by Davis (*Chem. News*, 1880, xli. p. 188); Lovett (*J. Soc. Chem. Ind.*, 1882, p. 110); Pringle (*ibid.*, 1883, p. 53). We here show the apparatus of Lindemann, as modified by Cl. Winkler, Fig. 125. The measuring-tube A is fitted at the top with a three-way tap, and has a capacity of 100 c.c., of which 25 c.c. are contained in the lower cylindrical portion, which is graduated in $\frac{1}{10}$ c.c. B is the absorption vessel filled with thin rods of phosphorus, and C the levelling bottle. The manipulation is the same as with the Orsat apparatus.

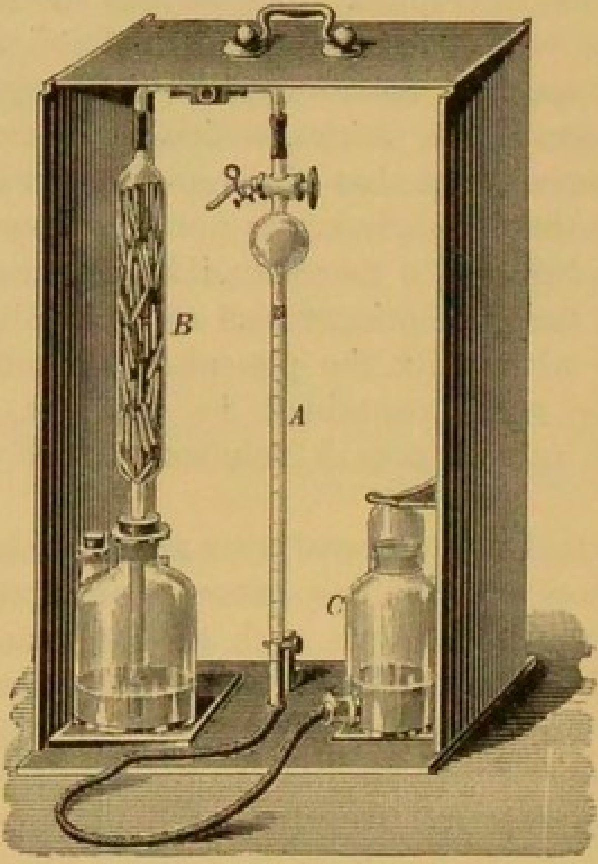

FIG. 125.

M. Liebig (Post's *Chem. Tech. Analyse*, 2nd ed., i. p. 700) describes an apparatus arranged for absorbing the oxygen by alkaline pyrogallol; the gas is aspirated by means of a rubber bellows into a 50 c.c. pipette, and forced from this through the absorbing solution into a graduated measuring-tube.

(b) *Examination for Acids.*—If only the *sulphur dioxide* remaining in the exit-gases is to be estimated, this cannot be done by the original Reich's method, owing to the presence of nitrogen oxides, but by Raschig's modification of that method (p. 244). Or else a measured volume of the gases is drawn through sodium hydroxide solution, which is afterwards strongly diluted with water and poured into chlorine- or bromine-water. This liquid is acidified with hydrochloric acid, heated to boiling, and barium chloride added. Each 1 g. of the precipitated barium sulphate indicates 93·77 c.c. SO_2 of 0° and 760 mm.

A *complete examination of the exit-gases* may be carried out as follows:—On the one hand the sum of the sulphur acids is determined, on the other hand the sum of the nitrogen acids, irrespective of the degree of oxidation. The following scheme agrees in the main with that adopted by the British Alkali Makers' Association in 1878; improvements have, however, been made in details (abridged from Lunge-Keane's *Technical Methods, etc.*, i. p. 336).

A small volume of gas is drawn continuously from the Gay-Lussac exits by means of a constant aspirator, at such a rate that at least 24 cb. ft. (=0·68 cb.m.) are collected in the twenty-four hours. The volume V drawn off is corrected in the way indicated *suprà*, p. 17, to 0° and 760 mm., and the corrected volume called V^1. The gas is drawn through four absorption bottles, each holding 100 c.c., and containing a column of liquid at least 75 mm. deep. The opening of the inlet tubes should not exceed 0·5 mm., as measured by a standard wire. The first three bottles each contain 100 c.c. of normal sodium hydroxide solution, free from nitre, the fourth 100 c.c. of distilled water. After the passage of the gases, the contents of the four bottles are combined, the bottles washed out with a small volume of water, and the total is divided into three equal parts, one portion being kept as a reserve. The first portion is titrated with normal sulphuric or hydrochloric acid, which gives a measure of the *total acidity* (SO_2, H_2SO_4, N_2O_3, and HNO_3). The second portion is added gradually to such a quantity of a warm solution of potassium permanganate, rendered strongly acid by sulphuric acid, that a slight excess of permanganate remains, which is finally neutralised by a few drops of sulphurous acid solution up to the point that only a faint rose tint remains. All the *nitrogen acids* are now present as nitric acid, no excess of sulphurous acid being in the solution. The HNO_3 is estimated by the well-known method of pouring it into 25 c.c. of a solution containing 100 g. crystallised ferrous sulphate and 100 g. pure sulphuric acid per litre, to which 20 to 25 c.c. pure concentrated sulphuric acid has been added, the operation being performed in a flask into which CO_2 is passed, the second tube of the stopper being luted with water; the flask is heated to boiling, and this is continued until the solution, which at first is dark-coloured owing to the nitric oxide present, has turned bright yellow. The ferrous salt remaining unoxidised by the nitric acid is retitrated with $N/2$ permanganate solution, equivalent to 0·004 g. oxygen per 1 c.c. The strength of the acid ferrous sulphate solution is compared each day with that of the permanganate solution. If x c.c. normal acid are used in the first titration (for total acids), y c.c. permanganate for retitrating the unoxidised ferrous salt, and z c.c. permanganate are equivalent to 25 c.c. of the ferrous sulphate solution, the figures required are obtained by the following equations (the volume V^1 being measured in cubic metres or in cubic feet):

(1) *Total acidity* expressed in grammes SO_3 per cubic metre =

$$\frac{0.120(100-x)}{V^1},$$

" " in grains SO_3 per cubic foot =

$$\frac{1.852(100-x)}{V^1}.$$

(2) *Sulphur* in grammes per cubic metre $= \dfrac{0.008(600-6x-z+y)}{V^1}$,

" grains " foot $= \dfrac{0.12346(600-6x-z+y)}{V^1}$.

(3) *Nitrogen* in grammes " metre $= \dfrac{0.007(z-y)}{V^1}$,

" grains " foot $= \dfrac{0{\cdot}10803(z-y)}{V^1}$.

Frantz (*Z. physik. Chem.*, 1904, p. 526) objects to this method that, owing to the action of oxygen and sulphur dioxide on the strongly alkaline solution of nitrate and nitrite, there is a formation of sulphate, sulphite, salts of sulpho-nitric acids, and nitrogen protoxide, whereby too little nitrogen oxides, an inexact figure for total acids, and too much nitrogen is found.

In most cases, in the place of the method just described, it is sufficient to determine *the total acidity of the gases* by titrating with decinormal sodium hydroxide solution and phenolphthalein, either by means of the absorbing bottle of Lunge (p. 324, Fig. 104), or that of the Alkali Inspectors (p. 245, Fig. 105), or a ten-bulb tube (p. 146, Fig. 72).

The maximum escape allowed under the English Alkali Act of 1906 is the equivalent of 4 grains SO_3 per cubic foot (=9·15 g. per cubic metre) of exit-gases, before they are mixed with air or smoke. In Germany the limit is 5 g. per cubic metre when burning pyrites, or 8 g. in the case of blende, all acids being calculated as SO_3.

The English Alkali Inspectors have recently adopted a mixture of 1 vol. *N*/2 alkali and 10 vols. neutral hydrogen peroxide for the absorption of acid gases. This overcomes the difficulty caused by secondary reactions between sulphites and nitrites, which is liable to occur when sodium hydroxide solution is used alone (Carpenter and Linder, *J. Soc. Chem. Ind.*, 1902, p. 1490).

Watson (*J. Soc. Chem. Ind.*, 1903, p. 1279) shows that the highest figures for acids are obtained, if the first absorbing vessels are charged with hydrogen peroxide alone, the following vessels with alkaline hydrogen peroxide; he attributes this to the decomposition of certain nitrogenous compounds by the hydrogen peroxide, which are only absorbed by alkaline hydrogen peroxide.

(c) *Nitric Oxide.*—This may be still present in the gases after they have passed through the above-described absorbing vessels. Its estimation has been described *suprà*, pp. 316 *et seq.*

(d) *Nitrogen Protoxide* has been found in the exit-gases by Inglis (*J. Soc. Chem. Ind.*, 1904, pp. 690, 778; 1906, p. 149; 1907, p. 668), and by Hempel (*Z. Elektrochem* 1906, p. 600). The methods for estimating this gas by combustion have been described, p. 314, but these are only applicable where it is present in somewhat considerable proportions. The extremely slight quantities of N_2O present in the Gay-Lussac exit-gases were determined by Inglis by cooling the gases with liquid air, fractionating the liquid at the lowest possible temperature, preventing any secondary reactions, and avoiding indirect analysis. His method showed much smaller proportions of N_2O than the similar process of Hempel, whose method was more indirect; it showed at most 10 per cent. of the loss of nitrogen to be in this form. These methods for estimating very little N_2O in the presence of large proportions of N, O, CO_2, nitrous gases, and SO_2 require such complicated apparatus and so much manipulative skill that they are outside of the domain of technical gas-analysis.

(e) *Loss of Sulphur in the Exit-gases.*—Lunge (*Dingl. polyt. J.*, 1877, ccxxvi. p. 634; *Sulphuric Acid and Alkali*, 4th ed., vol. i. p. 986) has drawn up a formula which allows the quantity of sulphur burnt, expressed in grammes per litre on the exit-gases, to be calculated from the percentage volume of oxygen in these gases. The loss of sulphur may be calculated by comparing this value with the quantity of sulphur acids present in the exit-gases. The formula is:

$$x = (20{\cdot}95 - a)0{\cdot}009637 \times \frac{1}{1{\cdot}00367t} \times \frac{h}{760},$$

where x signifies the total sulphur burnt expressed in grammes per litre on the exit-gas, a the percentage volume of oxygen in the exit-gas, t its temperature, and h the pressure.

Chlorine.

Free chlorine in gaseous mixtures can be estimated in various ways, mostly indicated in former chapters, *e.g.*, by absorption in a concentrated solution of ferrous chloride which absorbs the chlorine rapidly and in quantity, leaving air and carbon dioxide behind; the unchanged ferrous chloride is retitrated by standard permanganate, or by a solution of arsenious acid in sodium carbonate solution, retitrating with decinormal iodine solution and starch as indicator, in which case the hydrogen chloride present at the same time can be estimated as well (*cf.* p. 136).

The analysis of gases containing *a large percentage of chlorine*, *e.g.*, those evolved in the *Deacon process*, cannot be carried out by absorption in sodium hydroxide solution followed by titration for "available" and total chlorine, since it is impossible to avoid the formation of chlorate. This difficulty has been overcome by the following method, worked out in the laboratory of Messrs Gaskell, Deacon & Co. (Lunge's *Sulphuric Acid and Alkali*, 3rd ed., vol. iii. p. 470):—

Aspirate 5 litres of the gas, leaving the decomposer, through 250 c.c. of a sodium hydroxide solution of sp. gr. 1·075, divided between two or three bottles, to absorb both HCl and free chlorine. Unite the contents of the bottles, dilute to 500 c.c., and test as follows:

(1) One hundred c.c. of the solution are heated to boiling with 25 c.c. of a solution of 100 g. ferrous sulphate and 100 pure concentrated sulphuric acid in 1 litre of water, the heating being performed whilst excluding the air from the flask by a Bunsen valve or Contat bulb. When cold, the contents of the flask are diluted with 200 c.c. of water, and titrated with $N/2$ permanganate solution. The number of cubic centimetres so required we put $= y$, and the number of cubic centimetres of permanganate necessary to oxidise the 25 c.c. of ferrous sulphate solution $= x$.

(2) A small volume of sulphur dioxide solution is added to 10 c.c. of the above alkaline solution, and the mixture acidified with dilute sulphuric acid, so that there is a distinct smell of SO_2. The acidified solution is heated to boiling, allowed to cool, a few drops of permanganate solution added, if necessary, to oxidise any remaining sulphurous acid, after which the solution is neutralised with pure sodium carbonate and titrated with $N/10$ silver nitrate solution, employing neutral potassium chromate as indicator. z signifies the number of cubic centimetres of silver solution required. The percentage decomposition of the hydrochloric acid gas is then found by the expression $\frac{50(x-y)}{z}$, and the volume of air per 1 vol. of HCl by

$$\frac{43{\cdot}53+\frac{x-y}{8}}{z}.$$

Should some other volume of gas, n, be evaporated instead of 5 litres, the constant, 43·53, must be altered to $\frac{1{\cdot}624n}{50\times 0{\cdot}003645}$, assuming that the remaining operations are carried out exactly as above, and that 1 litre HCl at 0° and 760 mm. weighs 1·624 g.

Younger (*J. Soc. Chem. Ind.*, 1889, p. 88) prefers the following method: He passes the gas through a solution of arsenious acid, and employs an aspirator which gives the weight of chlorine in unit volume of the gases directly. The percentage of HCl in the gas is determined by titrating the reacting solution with silver nitrate. The absorption is effected in a cylinder containing 100 c.c. of an aqueous solution of arsenious acid, each 1 c.c. of which corresponds to 0·15432 grains (=0·01 g.) chlorine. The charged cylinder is connected with the bottle B (Fig. 126), containing about 1 g. potassium iodide dissolved in water; the arsenious acid solution is coloured blue by a very small quantity of indigo-carmine. A cubic foot (=0·0283 cb.m.) in capacity of the aspirator C is divided into any convenient number of parts, *e.g.*, 112. One side of the gauge-glass D is calibrated to give the grains of chlorine per cubic foot of gas, and the corresponding volume of gas aspirated is given on the other side of the same lines. The liberation of iodine from the potassium iodide solution, and the simultaneous bleaching of the indigo-carmine, indicate the completion of the test; when this occurs, the aspiration is interrupted, and the readings taken. The HCl is determined by titrating 10 c.c. of the arsenious acid solution with $N/10$ silver nitrate solution. Should the gases be free from HCl, the silver nitrate necessary for titration will be 28·2 c.c., this volume corresponding to the HCl derived from the chlorine absorbed. Any volume over and above this 28·2 c.c. corresponds to the HCl present as such in the gases. The way of calculating the results is illustrated by a special example in Lunge-Keane's *Technical Methods, etc.*, vol. i. p. 489.)

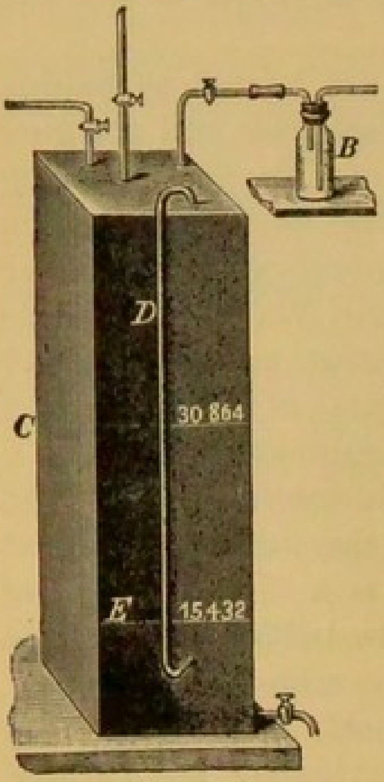

FIG. 126.

For estimating *very slight quantities of chlorine* in the air of certain chemical manufactures, or in that of their surroundings, a large quantity of this air is drawn through 15 to 20 c.c. of a freshly prepared colourless solution of potassium iodide, and then through a vessel containing decinormal sodium thiosulphate solution. In presence of free chlorine (or bromine) the potassium iodide solution is coloured brown by the liberated iodine. The solution is washed into a beaker, and the iodine titrated with *N*/10 or *N*/100 sodium thiosulphate; 1 c.c. *N*/10 sodium thiosulphate indicates 3·545 mg. chlorine (or 7·996 mg. bromine). The quantity of iodine vapour carried over from the first receiver into the sodium thiosulphate receiver is determined by titrating with *N*/100 iodine solution, and is added to the amount found in the first receiver.

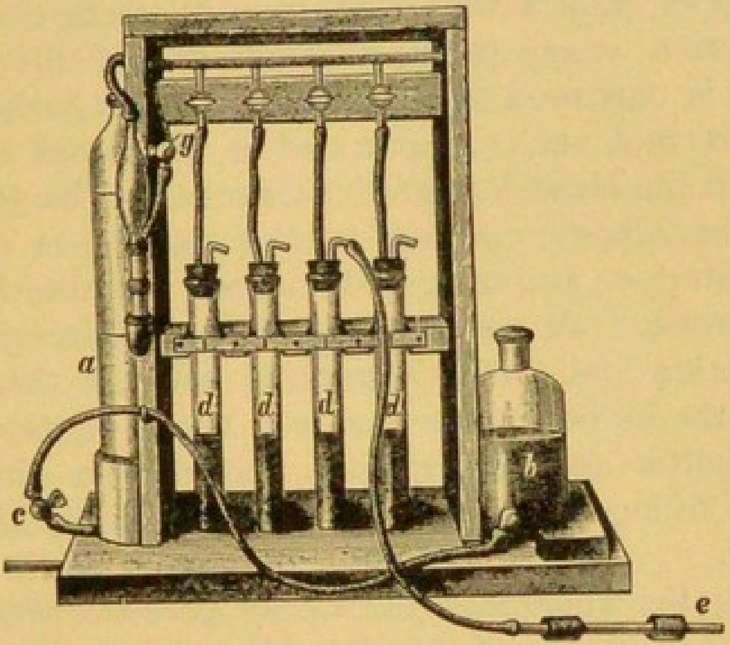

FIG. 127.

Such an estimation is especially necessary before opening bleaching-powder chambers, to prevent injury to the workmen, and nuisance in the neighbourhood. Before opening the chamber, the chlorine present in the air thereof must not exceed 5 grains per cubic foot (=11·5 g. per cubic metre), as agreed to by the manufacturers more than twenty years ago, but the present practice is to restrict the limits to 2½ grains per cubic foot.

The determination of the chlorine present in the chamber atmosphere may be carried out, *e.g.*, by an Orsat apparatus (p. 66). We here show in Fig. 127 the simplified apparatus described by Fleming-Stark (*J. Soc. Chem. Ind.*, 1885, p. 311). The burette *a* is filled with water and connected by means of a rubber tube with the reservoir *b*, a tap *c* being inserted between the two. This tap is provided with two passages at right angles to each other, the one of small and the other of large diameter. This allows of a strong flow of water when filling the burette, and of a diminished flow when the gas is forced into the absorbing solutions. The four tubes, *d*, *d*, *d*, *d*, are filled with an aqueous solution of potassium iodide, and each may be connected through a corresponding glass tap with the burette. Each absorption tube is provided with a double-bored stopper, and a tube reaching almost to the bottom of the absorption vessel passes through one of these openings. This tube is narrowed at its lower end, so as to break up the gas-bubbles, and at its upper end is connected through the tube *e* with the bleaching-powder chamber. The tube passing through the second opening in the stopper is cut off just below the stopper, and serves to connect the absorbing vessels to the burette. A small wash-bottle containing potassium iodide solution and starch is inserted between the absorption tubes and the burette. The two-way tap *g*, provided between the wash-bottle and the burette, permits the air to escape during the filling of the burette without passing through the wash-bottle.

In using the apparatus, 387 c.c. of gas, as measured in *a*, are drawn through one of the absorption tubes *d*; the solution in the wash-bottle affords an absolutely safe indication of the completion of the chlorine absorption. The contents of *d* are then washed into a beaker, and titrated with *N*/10 sodium arsenite solution. The grains of chlorine per cubic foot are obtained by multiplying by two the number of cubic centimetres of arsenite solution so required.

The Government Alkali Inspectors make use of the simple apparatus shown in Fig. 128. A is an ordinary rubber pressure ball, provided with a small hole B in the mouth-piece. The end of this passes through one of the two holes in the cork C; a glass tube D, bent at right angles, passes through the second. This latter tube reaches nearly to the bottom of the cylinder E, and is narrowed down at the lower end so that only a very fine needle can be inserted. The cylinder E is filled with the solution described below, and the outer end of D is inserted in an opening in the bleach at a height of 2 ft. above the floor. To take a sample of the chamber gas, A is compressed, the hole B being covered by the finger, and the pressure then released; by the expansion of the bulb the gas in the chamber is drawn through the tube D and the solution in E. The operation is repeated until the solution in E becomes coloured by the separation of iodine, and the number of aspirations to cause this is noted. Each delivery of the bulb corresponds to 4 oz. (about 100 c.c.) or $\frac{1}{250}$ of a cubic foot. The solution employed is prepared by dissolving 0·3485 g. of arsenious acid in sodium carbonate, neutralising with sulphuric acid, adding 25 g. potassium iodide, 2 g. precipitated calcium carbonate, 6 to 10 drops of ammonia, and diluting the whole to 1 litre; 26 c.c. of the solution are employed for each test, and a little starch solution is added as indicator. Under these conditions five deliveries of the bulb will produce a coloration when the gas contains 5 grains of chlorine per cubic foot, ten deliveries when the chlorine content is only 2½ grains per cubic foot, and so on.

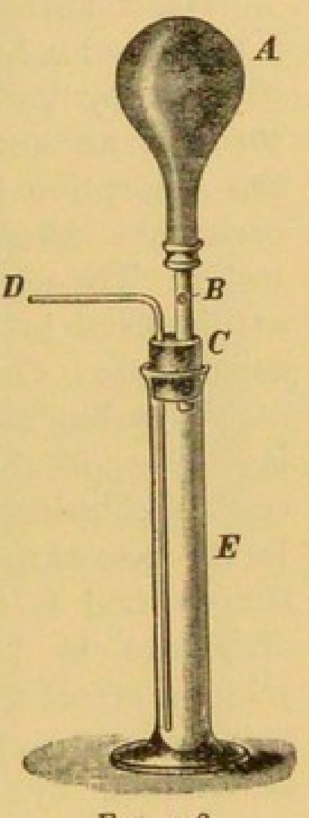

FIG. 128.

Orthotoluidine is recommended as a reagent for the colorimetric estimation of small quantities of free chlorine by Ellms and Hauser (*J. Ind. and Eng. Chem.*, 1913, p. 915; *Chem. Zentralb.*, 1914, i. p. 72). They prepare the reagent by dissolving one-tenth per cent. of orthotoluidine in a 10 per cent. solution of hydrochloric acid. The reagent does not deteriorate on standing. It produces with small quantities of chlorine a yellow colour, regardless of the soluble constituents of the water to be tested. The alkalinity of the water in no way affects the shade or tint produced. The presence of sulphates, chlorides, and nitrates of the alkalies and alkaline earths does not interfere with the test. The yellow colour develops in about three minutes and is permanent for at least half an hour. In this way 0·005 part per million of free chlorine can be detected. There is a good gradation of colour for increasing amounts of free chlorine.

Estimation of Carbon Dioxide in Chlorine Gas.

This estimation is very important, both in gas produced by the Deacon process, and in that produced by *electrolytical methods*, since carbon dioxide, if present to any appreciable amount, renders the manufacture of high-strength bleaching-powder impossible. Electrolytic chlorine sometimes contains up to 12 per cent. of carbon dioxide proceeding from the carbon electrodes.

Hasenclever (Winkler's *Industrie-Gase*, ii. p. 368) passes a measured volume of the gas, previously freed from hydrogen chloride by bubbling through a wash-bottle containing water, through an ammoniacal solution of barium chloride. When the absorption is complete, the solution is heated, the barium carbonate filtered off and thoroughly washed with boiled water. The washed precipitate is either ignited and weighed or dissolved in hydrochloric acid, and the barium precipitated as sulphate. One g. $BaSO_4$ corresponds to 0·1885 g. CO_2.

According to Sieber (*Chem. Zeit.*, 1895, p. 1963) this method is only applicable to gases containing not more than 10 per cent. of chlorine, a condition always satisfied by Deacon gases. In the case of more concentrated gases, like electrolytic chlorine, the method is unsuitable, owing to the solubility of barium carbonate in barium chloride. The object of boiling the solution before filtering off the barium carbonate is to destroy any carbonate present in the solution. The CO_2 can be also determined by absorbing the gases in sodium hydroxide solution, destroying the hypochlorite formed by addition of sodium arsenite, and then liberating the CO_2 by addition of sulphuric acid. This necessitates the previous determination of the CO_2 in the various reagents employed, and is also uncertain when only small amounts of CO_2 are present. Sieber therefore prefers absorbing the gases in a caustic soda solution of known carbonate content, decomposing the hypochlorite by boiling with cobalt oxide, adding sulphuric acid, and passing the liberated CO_2 through a solution of potassium iodide previously saturated with CO_2 and air, to retain any traces of chlorine carried forward; the purified CO_2 is then absorbed in a cooled potash bulb, and weighed.

This method is declared by Lunge (*cf.* Lunge-Keane., vol. i. p.

492) to be unreliable for the determination of small quantities of carbon dioxide, especially owing to the necessity of working with a solution of potassium iodide saturated with CO_2. It is both simpler and more accurate to absorb the gas in sodium hydroxide solution, to decompose the hypochlorite by boiling with ammonia, and then to estimate the CO_2 either by liberating the gas or by the barium chloride method.

Ferchland (*Z. Elektrochem.*, 1906, p. 114) takes away the chlorine by metallic mercury and then estimates the CO_2 by absorption in a solution of potassium hydrate.

Philosophoff (*Chem. Zeit.*, 1907, pp. 959 and 1256; Lunge and Berl, *Chemisch-technische Untersuchungsmethoden*, i. p. 584) gives special instructions for carrying out this process in a convenient manner.

Treadwell in his *Analytical Chemistry*, 6th ed., vol. ii. p. 694, describes a method for estimating the carbon dioxide in electrolytical chlorine, consisting in absorbing both chlorine and carbon dioxide by a solution of sodium hydroxide, measuring the residue, and titrating the hypochlorite formed in the alkaline solution by means of sodium arsenate, the difference representing the carbon dioxide. This method gives too low results, as appreciable quantities of chlorate are formed in the absorption of the chlorine. Hence Treadwell and Christie (*Z. angew. Chem.*, 1905, p. 1930) have modified the process as follows:—

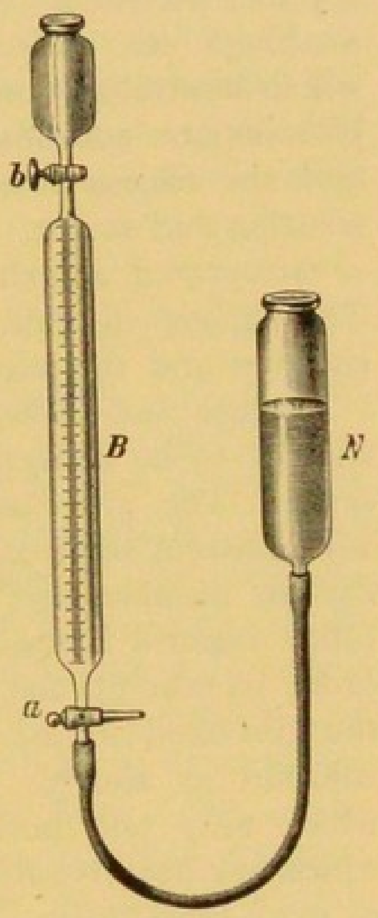

FIG. 129.

In Fig. 129, B is a Bunte burette, which is thoroughly dried before making a determination. The chlorine gas to be examined is dried by means of a calcium chloride tube, and is allowed to flow through B for from five to ten minutes before closing the taps. Then the lower three-way tap *a* is closed, then the upper two-way tap *b*, and the state of the thermometer and barometer noted. Now tap *a* is connected by the rubber tube with the levelling-tube N, filled with a sodium arsenite solution free from carbonate. This solution is prepared by dissolving 4·95 g. of arsenious oxide in dilute potassium hydroxide solution, adding phenolphthalein, exactly neutralising with sulphuric acid, and diluting to 1 litre. One hundred c.c. of this decinormal solution are introduced into the burette through tap *a* to absorb the chlorine, and subsequently 10 c.c. of a 1 : 2 potassium hydroxide solution through the funnel above *b*, whereby the CO_2 is absorbed. The residue of unabsorbed gas (nitrogen, oxygen, and carbon monoxide) as a rule amounts to 0·5 to 1 per cent. After taking the readings, the solutions and washings are collected, phenolphthalein is added, and the whole neutralised with hydrochloric acid; 60 c.c. of sodium bicarbonate solution (35 g. per litre) are then introduced, and the excess of arsenite solution titrated with $N/10$ iodine solution and starch. One c.c. $N/10$ arsenite solution consumed = 0·003546 g. chlorine, or 1·1016 c.c. chlorine at 0° and 760 mm. The carbon dioxide is found by the difference between the chlorine and the sum of $Cl+CO_2$ previously found.

Lunge and Offerhaus (*Z. angew. Chem.*, 1903, p. 1033) pass the gas to be analysed through two Bunte burettes placed in series. The gas contained in one of the burettes is treated with sodium hydroxide solution, to absorb both chlorine and carbon dioxide, and the residue measured. The gas in the other burette is treated with a potassium iodide solution in order to take up the chlorine, which is determined by titrating the liberated iodine with standard arsenite or thiosulphate solution as above. They also describe another method, in which only one burette is required for this determination, which has been modified by Treadwell and Christie (*ibid.*, 1905, p. 1930) as follows:—

The chlorine is absorbed by a 5 per cent. solution of potassium iodide, then the carbon dioxide by 10 c.c. potassium hydroxide solution, and the total volume of absorbed gas determined. The excess of KOH converts the liberated iodine into iodide and iodate. The liquid from the apparatus is then run into a beaker containing 10 c.c. of strong hydrochloric acid, and the liberated iodine titrated with thiosulphate. The results are accurate, but the method presents no advantage over the arsenite method as described above.

Lunge and Rittener (*ibid.*, 1906, p. 1853) absorb the chlorine in a Bunte burette by a $N/10$ solution of sodium arsenite and then the CO_2 by sodium hydroxide; the unchanged arsenite is titrated back, and the CO_2 obtained by difference from the volume of total absorbable gases found. The details of this method are also given in Lunge-Keane's *Technical Methods, etc.*, vol. i. p. 514.

Nourrisson (*Chem. Zeit.*, 1904, p. 107) examines such impure chlorine in an Orsat apparatus by first absorbing the chlorine by stannous chloride, then the carbon dioxide by sodium hydroxide, and finally the oxygen by metallic copper and ammonia solution.

Schloetter (*Z. angew. Chem.*, 1904, p. 301) absorbs the chlorine by hydrazine sulphate, whereby each 2 vols. of chlorine liberate 1 vol. of nitrogen, and subsequently the carbon dioxide by sodium hydroxide solution.

Detection and Estimation of Free Bromine and Chlorine.

Denigès and Chelle (*Bull. Soc. Chim.*, 1913, xiii. p. 626) employ an aqueous solution of magenta (rosaniline hydrochloride), decolorised by dilute sulphuric acid, and mixed with the same volume of acetic acid. This reagent is coloured yellow by chlorine, and purple by bromine. The coloured compounds formed can be extracted by chloroform. Their spectra are greatly different. This reaction allows of a colorimetric estimation of traces of free chlorine and bromine, in solution or in the state of vapour. (This process is an improvement of that described by Denigès in *Ann. Chim. anal.*, 1913, p. 8, where test paper soaked in a magenta solution, decolorised by bisulphite and acidified by weak hydrochloric acid, is employed.)

Impurities occurring in Atmospheric Air.

Apart from the normal constituents, oxygen and nitrogen, atmospheric air always contains various impurities in the shape of gases, vapours, mist, and dust. The determination of some of these has been already described in previous chapters; *e.g.*, dust and soot, p. 112; liquid admixtures (incl. moisture),[1]

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[1] The moisture contained in atmospheric air is usually estimated, not by chemical methods, but by the physical method of "psychrometry," which does not belong to the sphere of technical gas-analysis.

p. 115; carbon dioxide, pp. 69, 89, 96, 107, 136, 142, 222; ozone, p. 220; hydrogen peroxide, p. 221. Numerous impurities may, moreover, get into the air by industrial operations, *e.g.*, carbon monoxide, pp. 89, 109, 239; sulphur dioxide, pp. 135, 142 *et seq.*, 243 *et seq.*; hydrogen chloride, pp. 136, 145; chlorine, p. 136; hydrogen sulphide, p. 147; carbon disulphide, p. 314; inflammable gases and vapours, p. 316; nitroglycerine, p. 314; nitrogen oxides and acids, p. 314 *et seq.;* ammonia, p. 325; hydrogen cyanide, p. 328.

In this place we treat of some impurities carried into the air by specific chemical industries, apart from those already treated (mostly after Lunge-Keane's *Technical Methods*, vol. i. pp. 903 *et seq.*).

Phosphorus Trichloride.—Butjagin (*Arch. f. Hygiene*, xlix.) passes the air to be examined through a solution of sodium hydroxide, and estimates the sodium chloride formed by the reaction: $PCl_3 + 3NaOH = P(OH)_3 + 3NaCl$.

Fluohydric and Hydrofluosilicic Acid.—Traces of these acids occur in the air near aluminium works in which aluminium fluoride is used. This subject is treated in detail in a paper by H. Wislicenus (*Z. angew. Chem.*, 1901, pp. 701 *et seq.*), but he directed his efforts to the proof of the presence of fluorine compounds in the ashes of the plants affected by such air, without indicating a mode for testing for them in the air itself, which is evidently a matter of extreme difficulty. Where it is the question of testing gases for large quantities of those acids, and other acids are not present, or are separately estimated, the acidity of the gases, as determined by absorption in caustic alkali solution, with phenolphthalein as indicator, is a measure for them. Fellner (*Chem. Zeit.*, 1895, p. 1143) points out that the solution must be boiled, otherwise the results are too low.

Hydrogen Phosphide, H_3P, an extremely poisonous gas, occurs sometimes in slight traces in the air of laboratories or of factories. It can be detected by means of paper soaked with silver nitrate, which is thereby blackened by the secretion of metallic silver, phosphoric acid being formed. Its estimation when present as an impurity in commercial acetylene has been described *suprà*, p. 150.

Hydrogen phosphide can be estimated, according to Lunge (*Z. angew. Chem.*, 1897, p. 651), by passing the gases through bromine water or a solution of sodium hypochlorite, and precipitating the phosphoric acid thereby formed by magnesia mixture. If a silver solution is employed for absorbing it, the excess of silver must be first precipitated by hydrochloric acid. One mg. $P_2O_5 = 0{\cdot}48$ mg. H_3P.

According to Riban (*Comptes rend.*, lxxxviii. p. 581), hydrogen phosphide is absorbed by a solution of cuprous chloride in hydrochloric acid. Yokote (*Arch. f. Hygiene*, xlix.) estimates it by passing a large volume of the air either through nitric acid or through bromine water, and determining the phosphoric acid formed in the usual way. Volumetric methods are not applicable.

Hydrogen Arsenide, H_3As.—This gas is detected in the air by its characteristic garlic-like smell even when present in minute quantities; or by passing the air through a solution of silver nitrate, which is thereby darkened. Such a darkening is, of course, equally produced by hydrogen sulphide or phosphide. The same reagent can serve for the quantitative estimation of that gas, by precipitating the excess of silver with hydrochloric acid, and determining the arsenic in the filtrate as $Mg_2As_2O_7$.

$$2AsH_3 + 12AgNO_3 + 3H_2O = As_2O_3 + 12HNO_3 + 12Ag.$$

Mercury Vapour.

We have already in a former place (p. 115) mentioned the detection of this impurity in air by the grey coloration imparted to gold leaf, and its quantitative estimation by the same reaction.

Kunkel and Fessel (*Verh. d. phys.-med. Gesellsch.*, Würzburg, xxxii. p. 1) pass the dry air through a tube, 2 to 3 mm. wide and 25 cm. long, slightly bent in the middle, containing a few particles of iodine; a deposit of red or reddish-yellow mercuric iodide is formed just beyond the iodine, if any mercury vapour is present in the air, and its quantity may be approximately gauged. The air should not pass through the tube at a greater rate than 1 litre in from eight to ten minutes.

In order to estimate the mercury vapour quantitatively, the mercuric iodide, deposited as above, is dissolved in potassium iodide, filtered from any particles of solid iodine present, and sufficient sodium hydroxide added to the filtrate to combine with any free iodine. The mercury is then determined colorimetrically in the shape of the black sulphide by adding ammonium sulphide to the solution, and comparing the colour produced with that imparted to faintly alkaline solutions of mercuric chloride on similar treatment; or the mercury may be deposited by electrolysis and weighed (Lehmann, *Arch. f. Hygiene*, xx.). The maximum quantity of mercury vapour which can be present in 1 cb.m. of air at 0° is approximately 2 mg.; at 10°, 6 mg.; at 20°, 14 mg.; at 30°, 31 mg.

Ether Vapour.

This vapour may be absorbed quantitatively from an enclosed volume of air by sulphuric acid of sp. gr. 1·84 in about thirty minutes, and may thus be determined volumetrically (Horwitz, *Dissertation*, Würzburg, 1900).

Mercaptan.

Rubner (*Arch. f. Hygiene*, xix. p. 156) recommends as a qualitative test the grass-green coloration imparted by mercaptan to porous earthenware soaked with a solution of isatin in sulphuric acid; the air should be dried over calcium chloride, and then passed through tubes containing the pieces of earthenware. First a green, and then a bluish-green colour is produced. A quantitative determination in air is scarcely practicable; when lead nitrate is used as an absorbent, quantitative results are only obtained if very precise conditions are observed in regard to the concentration of the solution employed.

Aniline Vapour.

Lehmann (*loc. cit.*) passes the air to be tested for aniline through two absorption vessels in series, containing 10 per cent. sulphuric (not hydrochloric!) acid, neutralises the bulk of the acid and titrates the solution with bromine solution, the strength of which has been determined with potassium iodide and sodium thiosulphate. The bromine solution is prepared by dissolving 3 to 4 g. bromine in 1 litre of water, and adding sodium hydroxide until the colour of the solution is changed from brown to yellow. The bromine forms with aniline, tribromaniline. The reaction is :

$$3Br_2 + C_6H_5NH_2 = C_6H_2Br_3 . NH_2 + 3HBr.$$

One c.c. of $N/10$ bromine solution $= \frac{9 \cdot 3}{6} = 1 \cdot 55$ mg. aniline.

Tobacco Smoke.

Pontag (*Z. Unters. Nahr. u. Genussm.*, 1903, p. 646; Lunge-Keane, *Technical Methods, etc.*, p. 910) aspirates the smoke, first through caustic soda solution, then through sulphuric acid, and estimates therefrom the hydrocyanic acid and the nicotine, pyridine, and ammonia; also the carbon monoxide. As this subject does not exactly belong to technical gas-analysis, we refer to the above-stated publications.

The *injurious effects of the impurities of air*, both on account of the diminution they cause in the percentage of oxygen, and of their direct poisonous action, on health and vegetation, are described in Lunge-Keane, *loc. cit.*, i. pp. 908 *et seq.*, according to the investigations of Lehmann and of Haldane, founded on Government Reports.

Arndt's air-tester (Ger. Ps. Nos. 241074 and 247165; *J. Gasbeleucht.*, 1913, p. 407) shows the admixture of a certain gaseous impurity by the change of colour of a body impregnated with a test solution.

ANALYSIS OF GASEOUS MIXTURES PRODUCED ON A LARGE SCALE.

In the preceding chapters we have discussed all the methods applied in technical gas-analysis for the examination of gaseous mixtures produced on a large scale. In this place we shall merely enumerate the constituents present in such mixtures, and indicate the places where the analytical methods for them are described. The methods for taking proper samples of these gases have been described on p. 3 *et seq.*

1. *Fire-gases* (*Smoke-gases, Furnace-gases*).

Soot, p. 112.
Carbon dioxide, pp. 69, 89, 96, 107, 136, 142, 222.
Carbon monoxide, pp. 89, 109, 239.
Combustible gases, p. 309.
Sulphur dioxide, pp. 135, 142, 143.
Oxygen, pp. 55, 64, 69, 89, 152, 211.

2. *Producer-gases* (*including Water-gas*), *Dowson Gas, etc.*

Carbon monoxide, pp. 89, 109, 239.
Hydrogen, pp. 71, 90, 97, 109, 129, 152, 156, 167, 266.
Methane, pp. 71, 109, 152, 266.
Heavy hydrocarbons, pp. 117, 304.
Total combustible gases, pp. 155, 164.
Carbon dioxide, pp. 69, 89, 96, 107, 136, 142, 222.
Oxygen, pp. 55, 64, 69, 89, 152, 211.

3. *Coal-gas* (*Illuminating Gas*).[1]

Carbon monoxide, pp. 89, 109, 239.
Hydrogen, pp. 71, 90, 97, 109, 129, 152, 156, 167, 266.
Methane, pp. 71, 109, 152, 266.
Acetylene, pp. 118, 132, 147, 281.
Ethylene, pp. 109, 119, 167, 286.
Naphthalene vapour, p. 289.
Heavy hydrocarbons, pp. 117, 304.
Benzene, pp. 108, 167, 288.
Total combustible gases, pp. 155, 164.
Carbon dioxide, pp. 69, 89, 96, 107, 136, 142, 222.
Oxygen, pp. 55, 64, 69, 89, 152, 211.
Hydrogen sulphide, pp. 147, 150.

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[1] An historical study on the development of the analysis of illuminating gas has been published by Czakó in *J. Gasbeleucht.*, 1913, pp. 1192 *et seq.*

Carbon disulphide and other sulphur compounds, p. 147.

Total sulphur, pp. 149, 245, 247.

Tar vapours, p. 305.

Ferrocarbonyl, p. 313.

Ammonia, p. 325.

Cyanogen and compounds of it, p. 328.

Illuminating power, p. 210.

Specific gravity, p. 178.

Calorific power, p. 190 (according to *Chem. Trade J.*, 1914. p. 522, the House of Lords Committee has decided that in future the calorific value of the gas supplied to the customers shall be the only standard for its value).

COMPRESSED AND LIQUEFIED GASES.[1]

I. General Rules.—Such rules on the storage, carriage, sampling, etc., are contained in a document, communicated by the Prussian Minister of Commerce to the German Verein zur Wahrung der Interessen der chemischen Industrie, and published in *Chem. Ind.*, 1904, pp. 689 *et seq.*

The following gases are found in trade in the compressed or liquefied state: Carbon dioxide, ammonia, chlorine, sulphur dioxide, carbon oxychloride (phosgen), nitrogen protoxide, acetylene, marsh-gas (methane), coal-gas (including similar illuminating gases), hydrogen, oxygen, nitrogen and atmospheric air.

The original contains detailed descriptions of the vessels (bottles) serving for keeping and transporting these compressed or liquefied gases. These vessels, when filled, must not be thrown about, and should be protected against concussions of any kind; they must not be exposed to direct sunlight or other sources of heat, or to air of a temperature exceeding 40°.

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[1] This chapter is principally founded on the corresponding chapter in Lunge and Berl's *Chemisch-technische Untersuchungsmethoden*, 6th ed., 1910, i. pp. 638 *et seq.* The following special publications treat of this matter: Teichmann, *Komprimierte und verflüssigte Gase*, Halle, 1908; and Urban, *Laboratiumsbuch für die Industrie der verflüssigten und komprimierten Gase*, Halle, 1909.

The following table shows the properties and conditions of carriage of the more important liquefied and compressed gases :—

Gas, liquefied or compressed.	Sp. gr.			Vapour tension. Atmospheres.			Boiling-point at 760 mm.	Fusing-point.	Critical temperature.
	0°.	15°.	30°.	0°.	15°.	30°.	°C.	°C.	°C.
SO_2 . .	1·4350	1·3964	1·356	1·53	2·72	4·52	− 10·1	− 76	155·4
NH_3 .	0·6341	0·6138	0·5918	4·19	7·14	11·5	− 38·5	− 75	130·0
Cl_2 . .	1·469	1·4257	1·3799	3·66	5·75	8·8	− 33·6	− 102	146·0
CO_2 .	0·947	0·864	0·732	36·1	52·16	73·8	− 78·2	− 57	31·1
N_2O .	0·937	0·870	...	36·1	49·8	68·0	− 87·9	− 102	35·4
$COCl_2$.	1·432	...	...	...	...	...	+ 8·2	...	...
H_2 . .	...	...	...	...	...	...	− 252	...	− 234·5
O_2 . .	...	...	...	...	...	...	− 183	...	− 118·0

Gas, liquefied or compressed.	Critical pressure.	Sp. gr. at 0° and 760 mm. air = 1	Litre weight at 0° and 760 mm.	1 k. on being liquefied yields gas at 0° and 760 mm.	Conditions of carriage on German railways.		
					Official examination pressure.	Space required for 1 kg.	Repetition of the examination of pressure required after years.
	Atmospheres.			Litres.	Atmospheres.	Litres	
SO_2 .	78·9	2·264	2·9266	342	12	0·8	2
NH_3 .	115	0·597	0·7719	1290	30	1·86	4
Cl_2 . .	93·5	2·490	3·2191	310·5	22	0·8	2
CO_2 .	73	1·5291	1·9768	508·9	190	1·34	4
N_2O .	75	1·5298	1·9777	506	180	1·34	4
$COCl_2$.	...	...	...	...	30	0·8	2
H_2 . .	20	0·0696	0·08998	...	1½ times the full strength	...	4
O_2 . .	50	1·1055	1·4292	...		...	4

II. SAMPLING.—In most cases it is advisable to place the bottles horizontally before sampling. The bottles filled with such a liquid, when some of the gas has been taken out, have a gas space above the liquid the composition of which is not identical with the average composition of the liquid. Thus, *e.g.*, when analysing liquid carbon dioxide, there is an essential difference between the samples drawn from vertically or horizontally placed bottles. Werder (*Chem. Zeit.*, 1906, p. 1021), when analysing an inferior quality of liquid carbon dioxide, found on taking the sample (*a* from a bottle in the upright position 72 per cent., (*b*) from a bottle lying on its side 94 per cent. CO_2; in the case of very good qualities he found (*a*) 92 per cent., (*b*) 98·8 per cent.; in the case of a first-class article (*a*) 99 per cent., (*b*) 99·85 per cent. An analysis from a partly emptied bottle does not indicate the average composition (*cf.* Woy, *Chem. Zentralb.*, 1904, ii. p. 1072, and Wentzki, *ibid.*, p. 1763).

In the case of compressed or liquefied gases, standing under very high pressure, it is advisable to employ a *reducing-valve* for sampling. In order to remove all the air from it, the gas should pass for at least ten to fifteen minutes in a rapid current through the reducing-valve. In order to prevent the analytical apparatus from being smashed, Thiele and Deckert (*Z. angew. Chem.*, 1907, p. 737) warmly recommend interposing between the gas-bottle in this apparatus a glass Tee-piece, the descending branch of which dips into *mercury*. If the pressure in the apparatus exceeds that of the mercury column, the excess of gas escapes through the mercury into the air.

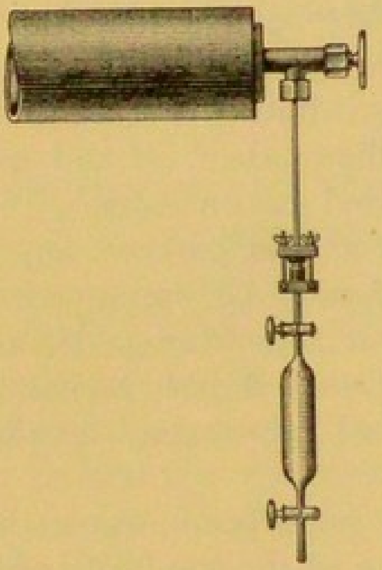

FIG. 130.

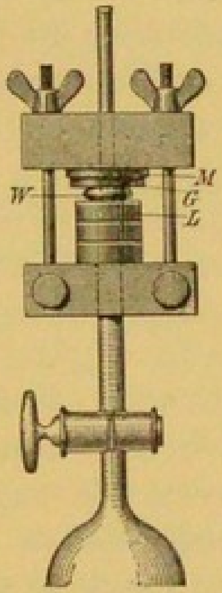

FIG. 131.

The sampling of liquefied gases can be in many cases advantageously performed by the pipette of Bunte and Eitner (*J. Gasbeleucht.*, 1897, p. 174, Figs. 130 and 131). On the lateral pipe of the bottle, which is placed in a horizontal or slanting position, a thin brass tube is fixed by means of a screw cap. At the other end of this tube there is a brass disc, M, with a leather or rubber washer, G. In order to firmly connect this tube with the pipette, the latter is provided at the top with a glass ring, W, ground flat, which can be pressed against G by means of a removable clamp with screw wings. The pipette holds 70 c.c., and is closed at top and bottom by well ground-in glass taps, which are not very conical, as they are in this case less easily forced out of the bores. For sampling liquid ammonia they are greased with castor oil. The pipette is accurately weighed on a chemical balance and fixed in the above-indicated manner to the gas-bottle. Then both taps are opened, in order to drive out the air from the pipette. Now the outer tap is closed, and by opening the valve of the gas-bottle, the liquefied gas is forced into the pipette until this is two-thirds full. It is recommended to put on gloves and protecting spectacles, to provide against the squirting about of liquefied gas on loosening the taps. When the filling has been done, first the valve of the gas-bottle is shut, then the second tap of the pipette, which is then taken off and weighed, so as to learn the quantity of liquefied gas enclosed.

3. *Measuring the Gas.*—For this purpose any of the gas-burettes previously described may be employed, such as the Bunte burette (p. 58), the Orsat apparatus (p. 66), and Hempel's apparatus (p. 82). For testing liquid carbon dioxide or chlorine, the most convenient apparatus is the "modified Winkler's burette" (p. 84).

As *confining liquids* are employed: water, or saturated solutions of salt (taking notice of the solubility of the gases in water, *suprà*, p. 31), or for more exact determinations mercury, in such cases where it is not acted upon by the gas to be tested. For chlorine we do not yet possess any suitable confining liquids.

Apparatus for examining Gaseous Impurities, not absorbed by the proper Absorbing Liquid for the Gas under Estimation.—Special contrivances have been described by Treadwell (*Quant. Analyse,* 4th ed., p. 606); Thiele and Deckert (*Z. angew Chem.*, 1907, p. 737); Franzen (*Z. anorg. Chem.*, 1908, lvii. p. 395); Stock and Nielsen (*Berl. Ber.*, 1906, p. 3389). Treadwell's apparatus is shown in Fig. 132. The thick-walled flask A, holding about 1½ litres, is charged with 500 c.c. of the absorbing reagent, and the absorbing tube with tap H is fixed air-tight in it. By sucking at H, the absorbing tube is entirely filled with absorbing liquid, whereupon H is closed. The Greiner-Friedrichs patent tap, I, is now turned into position II, and by sucking at its left-hand outlet pipe the entrance pipe is filled with absorbing liquid up to the plug of the tap. Now the tap is turned into position I, gas is passed on from the iron bottle until the air has been completely displaced, and the tap is put into position II, whereupon the gas enters into the absorbing tube. The non-absorbable gaseous constituents collect below H. Gas is passed into the apparatus until 70 to 80 c.c. non-absorbable gases have been obtained, which are driven over into a Hempel burette or other convenient apparatus, and analysed in the ordinary way.

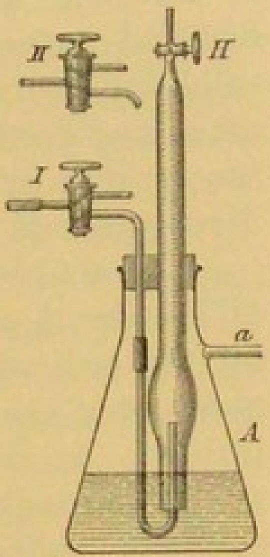

FIG. 132.

III. ANALYSIS OF THE VARIOUS DESCRIPTIONS OF COMPRESSED GASES.

(1) *Liquefied Sulphur Dioxide.*

The essential impurities present in this are: water, sulphuric acid, lubricating oil, air, sometimes also carbon dioxide.

In order to test for water, sulphuric acid, and lubricating oil, a good-sized sample of the liquid is taken by means of the Bunte-Eitner pipette, p. 359. This pipette is then placed upright in a large beaker, connected with weighed calcium chloride tubes, and by opening the tap on the side of the absorbing tubes the SO_2 is made to evaporate. When most of it has evaporated, the pipette is placed horizontally in an air-bath, heated to 70°, and the last remainder of volatile substances is forced through the absorbing tubes by means of a carefully dried current of air. The increase of weight of these tubes shows the percentage of water, which is especially important where the sulphur dioxide is to be employed for ice-producing machines, for, according to Lange (*Z. angew. Chem.*, 1899, pp. 275, 300, 595), a product containing water acts strongly on the steel valves of the compressors, especially at temperatures above 70°, with formation of ferrous sulphite thiosulphate.

The non-volatile residue remaining in the Bunte-Eitner pipette consists of sulphuric acid and lubricating oil. In order to estimate the *sulphuric acid*, the pipette is rinsed with distilled water, heated in order to remove the last traces of sulphuric acid, and the sulphuric acid titrated with standard alkali and methyl orange. The *lubricating oil* is obtained from the residue by extraction with ether, filtering the extract, and drying at 100°.

Any *air* present n the product is found by the apparatus of Treadwell, or of Thiele and Deckert (p. 360), and identified by the ordinary methods of gas-analysis. The non-absorbed gases may also contain a great portion of the *carbon dioxide* present. In order to estimate this more correctly, the gas is sucked through wash-bottles containing potassium dichromate solution, acidified by sulphuric acid. Here the sulphur dioxide is oxidised and retained, carbon dioxide and air escape, are dried by calcium chloride, and the CO_2 is absorbed in a weighed potash-bulb apparatus or by soda-lime.

In the case of liquid sulphur dioxide, employed in the manufacture of foodstuffs (*e.g.*, for saturating sugar solutions), sometimes a qualitative test for arsenic is called for. This can be performed by boiling the evaporation residue with sulphuric acid until all the SO_2 has been expelled, and testing the liquid in the Marsh apparatus.

In order to directly estimate the SO_2, the gas is passed into a Bunte burette (p. 58), or a modified Winkler burette (p. 84); a measured volume of decinormal iodine solution is allowed to go in, the burette shaken until the oxidation is complete, its contents run into an Erlenmeyer flask, rinsing several times with water, and the excess of iodine retitrated by $N/10$ thiosulphate solution. Each cubic centimetre of $N/10$ iodine solution consumed corresponds to 1·0946 c.c. of dry SO_2 at 0° and 760 mm.

A French patent, No. 435763, of the Comp. Ind. des Proc. R. Pictet describes an apparatus for the volumetric analysis of liquefied gases, especially sulphur dioxide.

2. *Liquefied Ammonia.*

According to Lange and Hertz (*Z. angew. Chem.*, 1897, p. 224), this may contain water, pyridine and its homologues, benzene, acetonitrile, ethyl alcohol, naphthalene, ammonium carbonate, and pyrrol; also lubricating oil from the compressors as a mechanical impurity.

In order to ascertain the quantity of *residue* remaining after the volatilisation, which is in most cases the only test required, Lange and Hertz employ the following simple method:—A glass tube of 30 to 50 mm. width is continued into a narrow tube of about 5 mm. width, holding at least 1·1 c.c. (Fig. 133). The tube holds altogether about 100 c.c.; up to a mark in the upper part 49 c.c., corresponding to 33·3 g. liquid ammonia. In the lower, narrow portion 1·1 c.c. is divided in 15 parts, so that each part corresponds to 0·2 per cent. NH_3, assuming the specific gravity of liquid ammonia at $-38° = 0{\cdot}68$, and that of the residue $= 0{\cdot}9$. At the bottom a piece of glass rod is fused on, so that the tube can be placed in a wooden stand or into the valve cap of the iron bottle.

In order to take a sample, the iron bottle is placed in a horizontal position and a small steel-tube screwed on to the valve. Now the valve is opened, and liquid ammonia is run into the sample tube up to the mark, which should take about one minute. The sample tube is closed with a nicked cork and its contents allowed to evaporate spontaneously, which takes about three hours. When the ice formed thereby has thawed off, and no more gas bubbles rise from the narrow tube, the volume of the residue in the narrow tube is read off. Each division indicates 0·2 per cent. This method yields rather too high results, for in taking the sample a little ammonia evaporates, so that the impurities relatively increase, and in the case of much water being present, some NH_3 remains in the residue. These errors are partly compensated by the fact that during the evaporation of the ammonia part of the impurities also volatilises.

FIG. 133.

In order to estimate the *pyridine* as well as the *ammonia*, a sample of the liquid ammonia is taken in the Bunte-Eitner pipette (p. 359). To the pipette, partially filled with the liquid ammonia, two Peligot tubes, charged with normal sulphuric acid, are joined, and by opening the intermediate tap of the pipette, ammonia is passed through these receivers, where it is retained by the sulphuric acid. In order to drive over the last portions of ammonia, at the end of the operation a current of air is passed through the apparatus. The sulphuric acid is diluted to 1000 c.c., and the ammonia and pyridine determined in this liquid. For this purpose so much of the acid liquid is measured off that it contains about 1·7 to 2 g. NH_3, diluted with water and titrated with normal ammonia and methyl orange, until the colour has just passed into pure yellow. The liquid, whose volume is now about 250 c.c., is distilled in a flask with cooler during half an hour, the lower end of the cooler dipping into 30 c.c. of water. All the pyridine and acetonitrile, together with some ammonia, is now in the distillate (A). To this a few drops of phenolphthalein are added, and it is titrated with normal hydrochloric acid, which indicates the ammonia quite sharply, as pyridine is quite neutral to phenolphthalein. When the liquid in the distilling flask has completely cooled down caustic liquor is added, and the ammonia, now set free, is distilled into normal acid, which is then retitrated. The acid now consumed, together with that consumed in the first distillation, indicates the quantity of ammonia; 1 c.c. normal hydrochloric acid = 0·01703 g. NH_3.

In the first distillate (A) the ammonia is exactly neutralised, a few drops of a 1 per cent. solution of patent blue, brand V.N., is added, and it is titrated with $N/2$ hydrochloric acid until the colour changes from pure blue into greenish-blue. This test is recommended by Milbauer and Stanek (*Z. anal. Chem.*, 1904, p. 215), who employ the following mode for the estimation of *pyridine.* The solution obtained by evaporating the liquid ammonia into sulphuric acid is evaporated nearly to dryness, put into a separating funnel, a sufficient quantity of freshly prepared solution of sodium bicarbonate and the same volume of ether added, and the whole shaken for ten to fifteen minutes in a mechanical agitator. The ether is poured off, fresh ether added, and the shaking continued for the same time. The united solutions of pyridine bases thus obtained are filtered through a filter moistened with ether, a few drops of patent blue solution added and thoroughly shaken up with an excess of decinormal sulphuric acid. Sodium chloride is added, and the liquid retitrated with decinormal caustic soda solution up to the reappearance of the blue colour. It is advisable to repeat the shaking out with ether a third time, and to convince one's self by titration that there is no more pyridine in solution.

The non-absorbable gases are collected and tested as described on p. 360.

3. *Liquefied Chlorine.*

In this product, which is made almost exclusively from electrolytic chlorine, there are found as impurities: air, carbon dioxide, carbon monoxide, and hydrogen chloride.

The chlorine gas is passed from the iron stock-bottle into a Bunte burette, or, preferably, into a modified Winkler burette (p. 84), and the real chlorine contained in it estimated by one of the well-known processes, *e.g.*, the potassium iodide or the sodium arsenite method, or by Ferchland's mercury method, mentioned on p. 349. The estimation of hydrogen chloride alongside of free chlorine is made by the methods described (pp. 136 and 142), that of carbon dioxide as described (p. 222). If chlorine, hydrogen chloride, and carbon dioxide must be estimated, all three, the chlorine is absorbed by mercury (p. 349), hydrogen chloride and carbon dioxide by caustic potash solution, the burette is emptied, the aqueous liquor separated from the mercury and the mercurous-chloride deposit; this is washed out, as well as the burette, and the chlorine ion titrated in the united solution, *e.g.*, by Volhard's method. One c.c. $N/10$ silver nitrate solution indicates 2·224 c.c. hydrogen chloride gas (at 0° and 760 mm.). The gaseous remainder not absorbed by the caustic potash solution is best collected in the apparatus of Treadwell or of Thiele and Deckert (p. 360); it consists of oxygen, carbon monoxide, and nitrogen, which are estimated as usual in technical gas-analysis.

4. *Liquefied Carbon Dioxide.*

In this occur: atmospheric air, or according to the mode of manufacture, various mixtures of oxygen and nitrogen; carbon monoxide, more rarely hydrogen sulphide, sulphur dioxide, empyreumatic substances; moreover: water, lubricating materials (glycerin, vaselin, or grease). Most of the liquefied carbon dioxide now found in the trade need not be tested for the last-named impurities. If, on evaporating it, glycerin is found in the residue, there is, according to Teichmann, ferrous bicarbonate present, which imparts a disagreeable taste to the water impregnated with such carbon dioxide. On passing the CO_2 through a strongly diluted, acidified solution of permanganate or of iodine, these reagents ought not to be decolorised, which would be caused by sulphur dioxide or empyreumatic matters. The latter would also be found by the brown coloration of concentrated sulphuric acid on passing the gas through it.

For a practical judgment on the quality of commercial liquid carbon dioxide it is mostly sufficient to estimate the content of the *liquid* portion in gases not absorbable by caustic potash. An enquiry into the air present in the *gaseous* space is mostly unnecessary. Only when very accurately enquiring into the quality of otherwise equal samples also the quality of the CO_2 present in the gaseous space need be examined. For establishing the contents of air in the gas taken from a bottle it is usually sufficient to test the carbon dioxide in the gas space before and after taking out the gas. The air-contents of the gas taken out will be approximately equal to the arithmetic mean of both tests.

Werder (*Chem. Zeit.*, 1906, p. 1021) employs for the analysis of liquid carbon dioxide an Orsat apparatus with a measuring-tube of 200 c.c. capacity and three absorbing-tubes, one filled with caustic potash solution, for absorbing CO_2; the second with alkaline pyrogallol solution, for absorbing oxygen; the third with ammoniacal cuprous chloride, for absorbing carbon monoxide. According to the quantity of the impurities, the measuring-tube is filled from ten to twenty times, always absorbing the CO_2 and testing the non-absorbed residue for oxygen and carbon monoxide. The same author enumerates the following rules for judging of the quality of commercial liquefied carbon dioxide: (1) The smell must be pure, not empyreumatic or irritating. (2) The taste must be purely acid. (3) The content of CO_2, taken from the bottle in a horizontal position, must be at least 98 per cent. (4) The content of carbon monoxide must not be above 0·5 per cent. (5) The gas must not contain either sulphurous or nitrous acid. (6) After passing it for a quarter of an hour through

100 c.c. of warm *N*/100 permanganate solution, acidulated with sulphuric acid, there must be sensible decolorisation. (7) After passing the gas for a quarter of an hour through 100 c.c. of *N*/100 silver nitrate solution, acidified with nitric acid, there must be no precipitate visible.

For estimating the percentage of *air* in liquid carbon dioxide any gas-analytical apparatus may be used. Lange (*Chem. Ind.*, 1900, p. 530) for this purpose employs a modification of the Winkler gas-burette, constructed by himself and Zahn, and shown *suprà*, p. 55, where also its manipulation is described. Wentzki (*Z. angew. Chem.*, 1913, i. p. 376) describes for this purpose an apparatus consisting of a burette with two taps, below which there is a measuring vessel and two level-bottles, one of which contains caustic potash, the other mercury. The bottom tap of the burette is also connected with the carbon dioxide vessel, and a bubble-counter. The apparatus is manufactured by Dr Bachfeld & Co., of Frankfurt a. M.

An investigation of the thermal properties of carbon dioxide at low temperatures (+20° to −50° C.) has been made by Jenkin and Pye (*Proc. Roy. Soc.*, 1913, March; *Chem. Trade J.*, 1913, lii. p. 260).

5. *Liquefied Nitrogen Protoxide.*

This product is sold especially for medical purposes. The impurities prejudicial to this employment, as nitric oxide, chlorine, acid gases, and ammonia, should be removed before compression by washing with ferrous sulphate solution, caustic potash, and weak acid. The methods for estimating the nitrogen protoxide itself have been described *suprà*, p. 314.

6. *Compressed Hydrogen.*

The essential impurities of electrolytically produced hydrogen are: oxygen (admissible maximum content = 2 volume per cent.) and nitrogen. Hydrogen produced in other ways may contain arseniuretted hydrogen, carbon monoxide, and carbon dioxide. For testing qualitatively for arseniuretted hydrogen, Reckleben and Lockemann (*Z. anal. Chem.*, 1908, p. 126; *Z. angew. Chem.*, 1908, p. 433) pass the gas through a 5 to 10 per cent. ammoniacal silver nitrate solution. In the presence of AsH_3 the solution is blackened by precipitated silver, and the arsenic can be proved in the solution by means of ammonia as silver arsenite.

7. *Compressed Oxygen.*

The commercial article may contain hydrogen (admissible maximum content=4 volume per cent.), carbon dioxide, and nitrogen. The analysis takes place according to the prescriptions given in previous chapters. Murschhauser (*Z. angew. Chem.*, 1908, p. 2503) describes a special apparatus for the analysis of compressed oxygen of high percentage.

GAS-VOLUMETRIC ANALYSIS.

Gas-volumetric analysis comprises those operations in which a constituent of a solid or liquid substance is determined by the generation and measurement of a gas. In some instances, air displaced by the generated gas is measured instead of the latter.

We now describe the methods and apparatus belonging to this chapter.

THE AZOTOMETER.

This instrument was designed by Knop in the year 1860 for the determination of ammonia, by the decomposition of its salts with sodium hypobromite and measurement of the liberated nitrogen. It has been improved by P. Wagner (*Z. anal. Chem.*, 1870, p. 235; 1875, p. 247). It can also be used for other gas-volumetric purposes, in which gases are measured over water, as proposed by Baumann (1890) and others.

This apparatus is shown in Fig. 134. The reagent employed is a sodium hypobromite solution, prepared as follows:—One hundred g. sodium hydroxide are dissolved in water and diluted to 1·25 litres; 25 c.c. bromine is added, with external cooling by water, the whole well shaken, and finally cooled. The solution must be kept in the dark in a well-stoppered bottle. It is employed in the bottle A, on to the bottom of which the glass cylinder *a* is fused. This bottle stands in the large glass vessel, B, which serves for cooling A after the decomposition. A is closed by a tightly fitting rubber stopper, through which passes the glass-tap tube *f*, which is connected by the rubber tube *e* to the first of the communicating tubes *c* and *d*. These tubes are placed in the cylinder C, filled with water, and containing

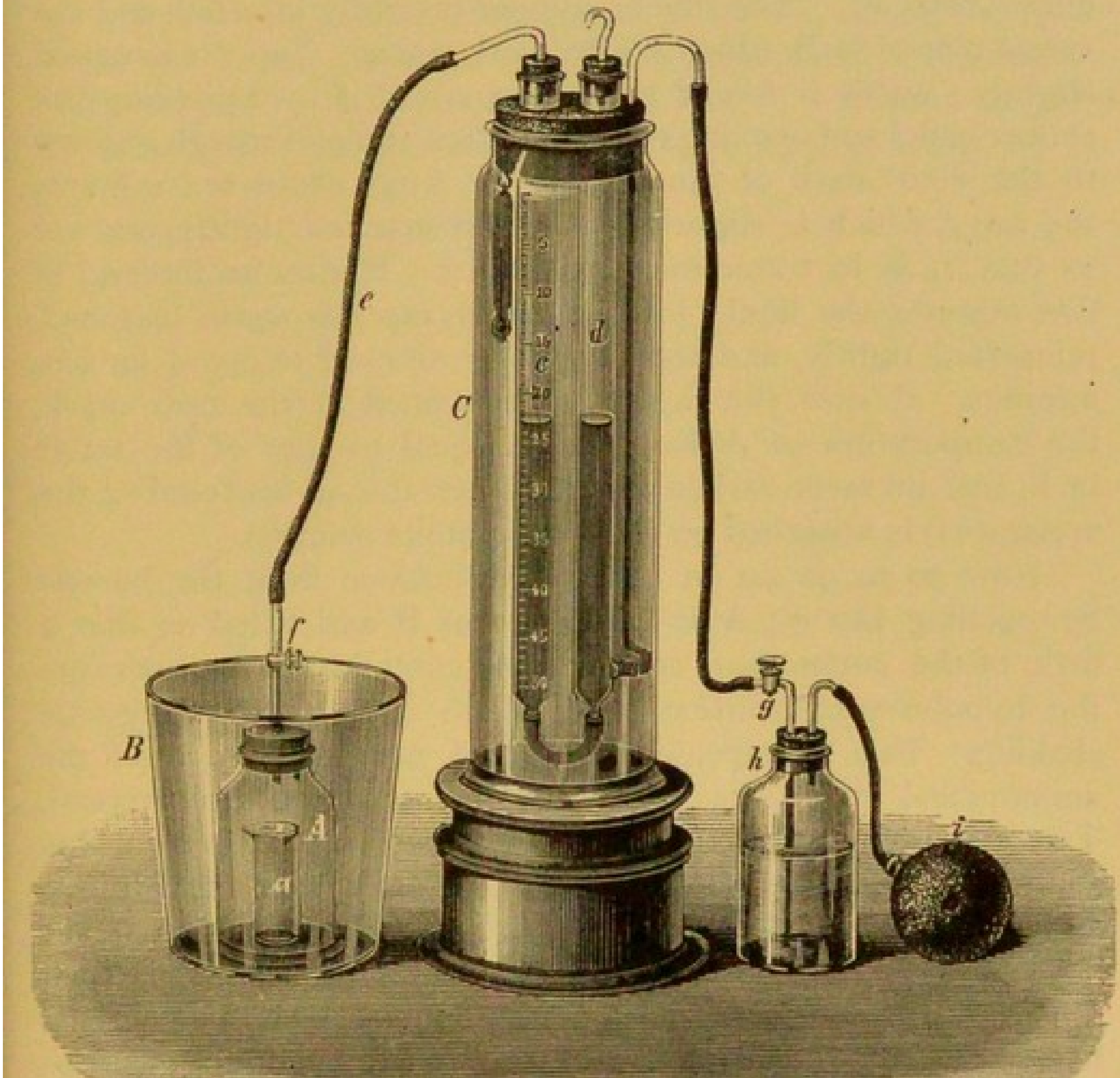

FIG. 134.

also a thermometer. Tube *c* is a gas-burette, holding 50 c.c.; *d* is the level-tube, connected at the top by a rubber tube with glass-tap *g* to the supply vessel *h*. This vessel and the tubes *c* and *d* are filled with water, which may be slightly coloured to facilitate the reading.

The determination of the ammoniacal nitrogen is made as follows:—The reaction taking place is

$$2NH_3 + 3NaOBr = N_2 + 3NaBr + 3H_2O.$$

Ten c.c. of the ammonium salt to be tested are introduced into the inner vessel *a*, and 50 c.c. of hypobromite solution into the outer vessel A. The rubber stopper is tightly inserted, and the vessel placed in B, which is filled with water. Tap *f* is loosened slightly; water is forced into pipes *c* and *d* by squeezing the rubber ball *i* and opening tap *g*, and then run off through *g* down to the zero mark of the burette *c*. After about ten minutes the tap *f*, which is slightly greased, is inserted tightly, and set so that A is in communication with *c*. If after an interval of five minutes the liquid in *c* has risen, tap *f* is again loosened, reinserted tightly, and the apparatus allowed to stand for five minutes. If now the liquid has remained at the zero mark, the temperature of A has become equal to that of the water in B, and no more carbon dioxide (from the air enclosed in the apparatus) is absorbed by the hypobromite solution.

Now 30 to 40 c.c. of this are withdrawn from the burette by opening tap *g*; A is taken out of B and tilted so that a little of the ammonium salt solution contained in *a* flows into the hypobromite solution, with which it is mixed by gentle shaking. This is repeated until the greater portion of the ammoniacal liquid has been poured out and decomposed. Tap *f* is then closed, the bottle A is thoroughly shaken, *f* is again opened to let the generated nitrogen pass over into *c*, and this is repeated until the water in *c* remains at a constant level; usually it is sufficient to shake three times. A is then replaced in B. After from 15 to 20 minutes, A and its contents have acquired the temperature of the water in B, and the gas contained in *c* that of the water in C. Tap *g* is then opened until the water is at the same level in *c* and *d*; the volume of the nitrogen in *c*, the temperature of the water in C, and the barometric pressure are noted.

From these data the weight of the nitrogen can be calculated, taking notice that the reaction as formulated *suprà* is not quite complete (possibly owing to the formation of hydrazine), according to Raschig (*Chem. Zeit.*, 1907, p. 926). Dietrich has published tables for converting the observed volumes of nitrogen into weights, allowing for that incompleteness of the reaction. These tables are given in Lunge-Keane, pp. 128 to 130, but not repeated here, because, as shown by Classen (*Ausgew. Methoden*, ii. p. 501), they are founded on an incorrect litre-weight of nitrogen. They are, moreover, unnecessary, since Lunge has shown (*Chem. Ind.*, 1885, p. 165) that that incompleteness of reaction can be correctly compensated by increasing the values obtained by 2·5 per cent., which is simply done by calculating for each cubic centimetre of the nitrogen obtained (reduced to 0° and 760 mm.): 0·0012818 g. N = 0·001558 g. NH_3.

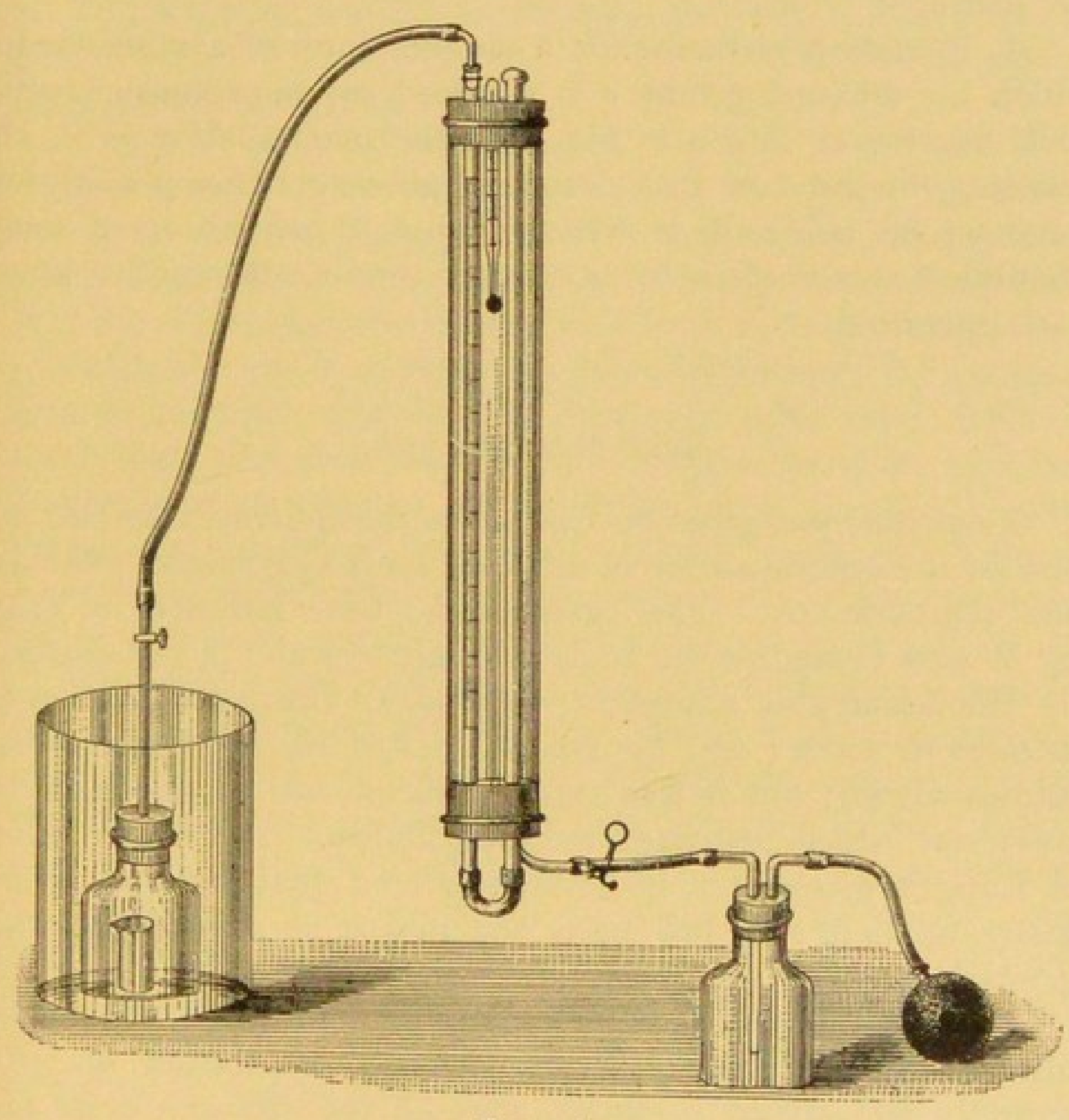

FIG. 135.

When testing for *urea*, which is decomposed in the azotometer by the reaction:

$$CO(NH_2)_2 + 3NaOBr = 3NaBr + CO_2 + N_2 + 2H_2O,$$

Lunge observed a minus engagement of nitrogen of the amount of 9 per cent.; each cubic centimetre of nitrogen (at 0° and 760 mm.) therefore indicates 0·002956 g. urea.

When using the azotometer, it is particularly important that the temperature in the generating vessel A and the measuring-tube *c* should remain constant during the whole experiment. If vessel A holds 150 c.c., a temperature variation of 1° causes an error of 0·5 c.c., and a variation of 2°, an error of about 1 c.c. Such errors of course influence the results considerably, especially if only small quantities of gas are liberated.

A. Baumann recommends a simpler form of azotometer in which the measuring-tube *c* is replaced by an ordinary pinchcock burette, as shown in Fig. 135; the manipulation is in all respects the same as that described above. If many analyses have to be made, it is well to employ two or three such simplified azotometers, so as to save time for the cooling after each operation.

THE NITROMETER.

This name was given by Lunge[1] to the apparatus devised by him for the determination of nitrogen acids by means of mercury and sulphuric acid. This reaction had been indicated in 1847 by Walter Crum, for the analysis of nitrates and of gun-cotton; by Frankland and Armstrong in 1868, for the determination of nitrates in water; and by Davis in 1878, for the valuation of nitrous vitriol; but it was rather difficult and troublesome to carry out, which restricted its applicability. The construction of Lunge's nitrometer, however, rendered that reaction to be easily applied, and has been the means of bringing it into general use.

If nitric acid or solutions containing a nitrate or nitrite, or nitroso-sulphuric acid ("nitrous vitriol"), are shaken up with mercury and strong sulphuric acid, all the nitrogen acids are reduced to nitric oxide, which is measured, and from the volume of which the weight of the compound tested for is calculated.

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[1] *Ber.*, 1878, p. 174; 1895, pp. 1878 and 2030; 1888, p. 376, and in many other publications.

First an unstable substance of blue colour makes its appearance, which was first observed by Lunge, and later on examined by Sabatier (*Bul. Soc. Chem.*, 1897, p. 782), Trautz (*Z. physik. Chem.*, 1903, p. 601), Raschig (*Z. angew. Chem.*, 1905, p. 1303), Lunge and Berl (*ibid.*, 1906, p. 807). On the strength of these investigations the reaction in the case of nitric acid can be formulated as follows:—

(1) $2HNO_3 + 2Hg_2 + 4H_2SO_4 = 2Hg_2SO_4 + 4H_2O + 2SO_5NH$ (nitroso-sulphuric acid).

(2) $2SO_5NH + Hg_2 + H_2SO_4 = Hg_2SO_4 + 2SO_5NH_2$ (nitrosi-sulphonic acid, blue compound).

(3) $2SO_5NH_2 = 2H_2SO_4 + 2NO$.

In the method as orginally devised, and frequently carried out up to this day, the mercury, which serves as confining liquid, itself takes part in the reaction. It has, however, been found that the nitrometer serves very well for a variety of other cases, in which the gas in question is given off without the co-operation of mercury, and is only measured over this. Both for these purposes, but also for the original reaction of Crum, Lunge later on effected the liberation of the gas in a separate vessel, and measured the gas over dry mercury. Later on Lunge developed from the nitrometer his "Gas-volumeter," which has been already described *suprà*, pp. 21 *et seq.*

The widely extended applicability of the nitrometer is mainly due to the following reasons:—In the first place, most gases, even those which are soluble to a considerable extent in water, can by its means be measured over mercury without the use of a mercury trough, which previously was always necessary for this purpose. The apparatus is simple, requires but little mercury, and is easy to manipulate and to shake. Secondly, it is equally suitable for those cases in which the gas is evolved and measured in a pure state, or for those in which it is liberated in a separate vessel and the displaced air measured. It can also be used for ordinary gas-analysis, and for determinations in which a gas, generated from a solid or liquid substance, has to be separated from other gases as in the determination of carbon dioxide by Lunge and Marchlewski's method, etc.

Böckmann (3rd ed., i. p. 63), in describing the nitrometer, says :—

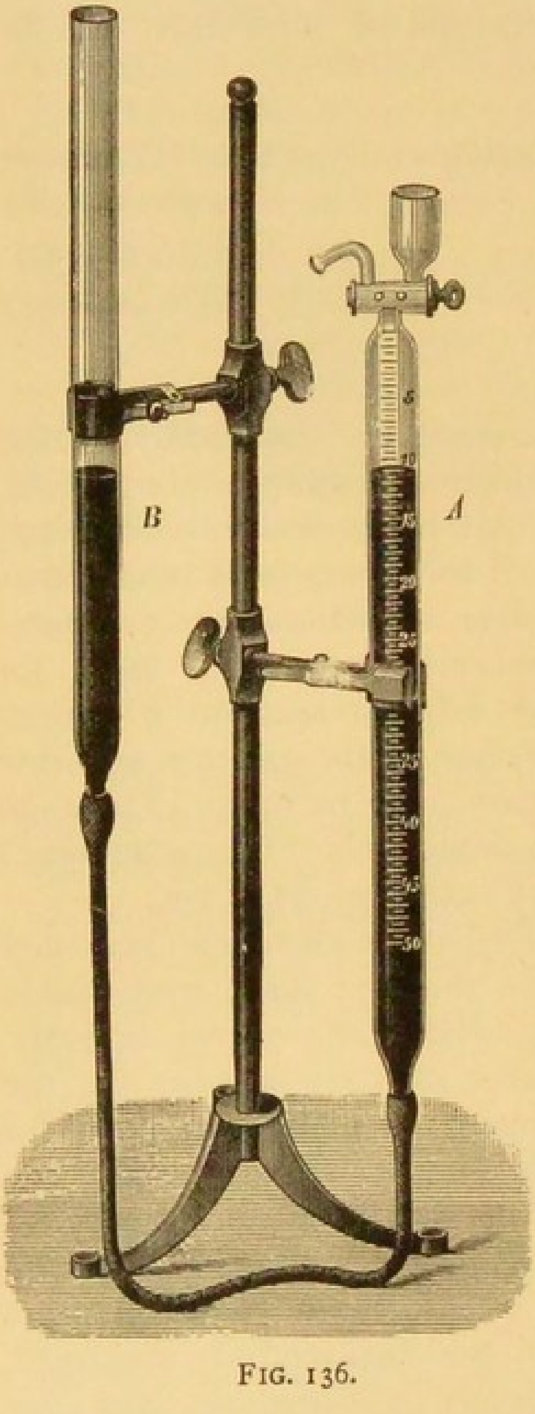

FIG. 136.

"Lunge's nitrometer, in its various modifications, is an exceptionally valuable apparatus, and is therefore very largely used for technical work. There is scarcely another apparatus for technical analysis which has so many practical applications, and is at the same time so easily handled. Those of its applications which have been published are numerous; those which are unpublished, and which are carried on in every technical laboratory, are certainly still more numerous."

The nitrometer is shown in Fig. 136 in its original form, as still used in most cases for the analysis of nitrous vitriol in the sulphuric acid industry, and for many other purposes. Tube A has a capacity of 50 c.c.; it is drawn out at the bottom and graduated in 1/10 c.c. The graduation starts immediately below the three-way tap which terminates the tube at the top. This tube may either have a vertical and an axial passage, as in Winkler's or Bunte's gas-burettes, or it may be a Greiner and Friedrichs tap with two oblique passages, as shown in its three positions in Fig. 137 A, B, C. The latter form closes more tightly, and is more easily manipulated, than the former, and is therefore usually attached to the newer forms of apparatus. Above the tap, a beaker-shaped funnel and a side-tube, *d*, are placed. In position A the measuring-tube communicates with *d*; in position B, with the beaker; in position C the tap is closed.

The measuring-tube A, Fig. 136, is connected by thick-walled rubber tubing with the level-tube B. The latter is a simple cylindrical glass tube of the same diameter as A, and drawn out at the bottom for attaching the rubber tubing. Both A and B are held by clamps, in which they can be moved.

To use the apparatus, for instance for the assay of nitrous vitriol, tube B (Fig. 136) is placed so that its lower end is somewhat higher than the tap on A, and mercury is poured in through B, the tap on A being open, until the mercury enters the beaker on A; as this takes place from below, no air-bubbles are formed on the sides of the tube. The tap is then closed, the mercury in the beaker-funnel allowed to flow out through the side passage of the tap, tube B lowered, and the tap closed. The nitrous vitriol is then run into the funnel from a 1 c.c. pipette, divided into $\frac{1}{100}$ c.c.; in the case of very strong nitrous vitriol 0·5 c.c. are used for each test, in that of weak vitriol 2 to 5 c.c. The level-tube B is then lowered, the tap carefully opened, and the acid drawn into tube A, care being taken that no air gets into this tube. The funnel is then rinsed with 2 to 3 c.c. of sulphuric acid, free from nitrogen acids, which is similarly drawn into tube A, and the washing repeated with another 1 to 3 c.c. of sulphuric acid. The reaction is then started by removing A from the clamp, and thoroughly mixing the acid with the mercury, by repeatedly holding the tube almost horizontally, taking care that no acid gets into the

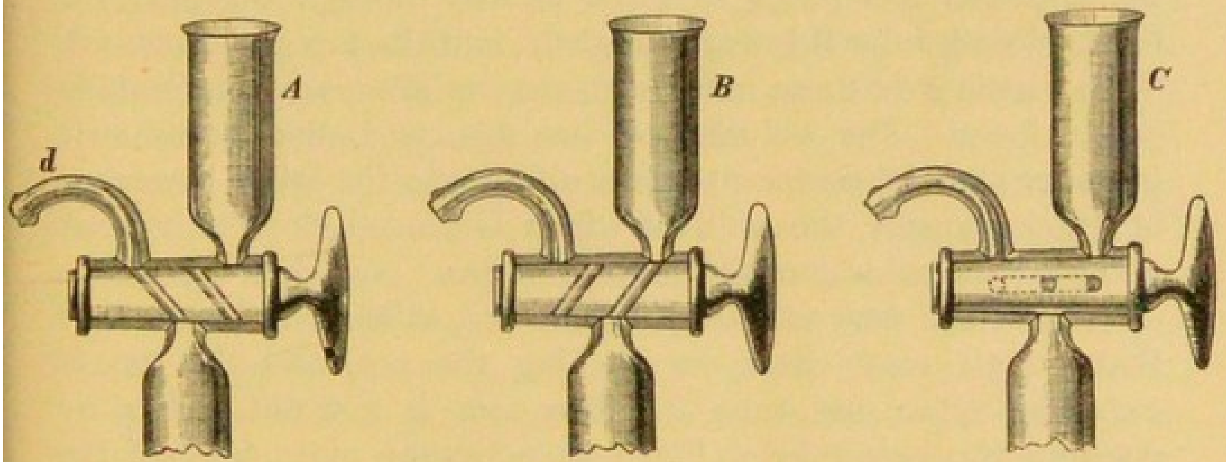

FIG. 137.

rubber tubing, and then sharply raising it to a vertical position. It is then shaken for one or two minutes, until no more gas is evolved.

The two tubes are then placed so that the mercury in B is as much higher than that in A as is necessary to compensate for the height of the acid in the latter; 1 mm. of mercury is allowed for every 6½ mm. of acid. After the temperature has become equalised, the pressure is exactly adjusted by pouring a little acid into the funnel and cautiously opening the tap. If the gas is under diminished pressure (which is preferably aimed at in the manipulation), acid will flow from the funnel into A; the tap is at once closed before air can enter, and the operation repeated after raising tube B very slightly. If, on the contrary, the enclosed gas tends to force its way through the acid, the tap is closed, tube B lowered slightly, and the tap again opened. With a little care these manipulations can always be successfully carried out. The volume of the gas, and the barometric pressure and the temperature are observed; the latter by means of a thermometer, the bulb of which is placed close to tube A and near the middle of the column of gas.

When the determination is finished, tube A is lowered, so that no air may enter on opening the tap, and the gas is expelled by raising tube B. The acid is got out, either by opening the side-tube *d* (Fig. 137), or in the older form of the tap through the axial passage, and the last traces are removed by means of filter paper. The nitrometer is then ready for the next determination.

To make sure that the tap on tube A fits tightly, it is greased with a little vaseline, taking care that none of this gets inside the tap so as to come into contact with the acid, which would lead to the formation of very badly settling froth.

No glass tap can be expected to keep perfectly tight for prolonged time when exposed to considerable variation of pressure. A tap can, however, be regarded as satisfactory, if no air-bubble is visible at the top of the tube after filling it completely with mercury, and lowering tube B during an interval of two hours. Superior to the ordinary ground-in glass caps are the taps provided with a mercury seal, as described by Göckel in *Z. angew. Chem.*, 1900, pp. 961 and 1238 (sold by Alt, Eberhard and Jäger, of Ilmenau in Thuringia).

The volume of the nitric oxide found by means of the nitrometer is reduced to 0° and 760 mm. pressure in the ordinary way. Each cubic centimetre of NO in the "normal" state corresponds to 1·3402 mg. NO, or 0·6257 mg. N_2, or 1·6975 mg. N_2O_3, or 2·8143 mg. HNO_3, or 5·3331 mg. nitric acid of 36° Bé., or 4·5472 mg. nitric acid of 40° Bé.

The determination of the total nitrogen percentage of nitrates or nitrites soluble in water is carried out similarly. In such cases, where a solid, soluble in water, is analysed, the weighed substance is introduced into the funnel of tube A, dissolved there in a very small quantity of water, the solution drawn into the tube, the funnel rinsed with concentrated sulphuric acid, and the decomposition carried out as above described.

The concentration of the sulphuric acid in the nitrometer must be kept within certain limits up and down. Acids containing more than 97 per cent. H_2SO_4, when shaken with mercury, give off sulphur dioxide, and must therefore not be employed. The solubility of nitric oxide in sulphuric acid increases with the concentration of the latter. Acid of 96 per cent. H_2SO_4 dissolves 3·5 volume per cent. NO; acid of 90 per cent., 2; of 80 per cent., 1·1 volume per cent.; that is: 10 c.c. sulphuric acid of 96 per cent. H_2SO_4 keeps 0·35 c.c. NO in solution, and so forth (Lunge, *Ber.*, 1885, p. 1391; Nernst and Jellinek, *Z. anorg. Chem.*, 1906, xlix. p. 219; Tower, *ibid.*, 1906, l. p. 382). Hence, for correct analyses a correction must be made for the nitric oxide dissolved, which is not required for more dilute acids. On the other hand, the employment of acids below 75 per cent. H_2SO_4 gives rise to the formation of grey mud, consisting of mercury and mercurous sulphate, which makes it impossible to take accurate readings. The correction of the nitrometer readings for the nitric oxide dissolved in the liquid is also treated by Joyce and La Tourette in *J. Ind. Eng. Chem.*, 1913, p. 1017.

In the analysis of *substances insoluble in water*, but soluble in concentrated sulphuric acid, more especially dynamites and pyroxylins, for which purpose the nitrometer is now nearly always used, the solution in sulphuric acid is also carried out in the beaker-funnel. In this case, in order to avoid loss of nitrous fumes, the device proposed by Lunge (*Chem. Ind.*, 1886, p. 274), as shown in Fig. 138, is used. The beaker-funnel of the nitrometer is closed by a rubber stopper, provided with an S-tube, ending above in a small funnel. The substance is placed in the beaker, and concentrated sulphuric acid introduced through the small funnel. The S-shaped bend of this tube remains full of sulphuric acid, which prevents the escape of nitrous fumes, and which flows into the beaker, when the acid in the latter is drawn into the measuring-tube A.

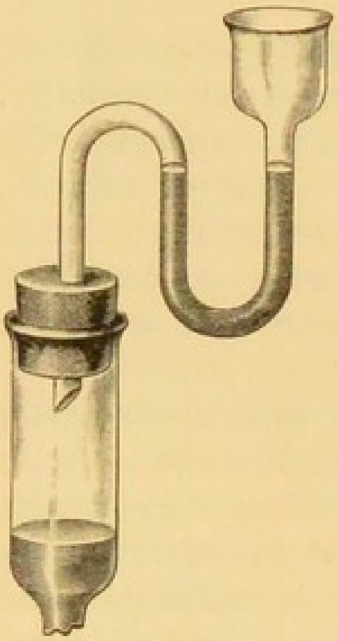

FIG. 138.

It is immaterial whether in the dissolving operation an insoluble powder, such as kieselguhr in the case of dynamite, or some undissolved saltpetre, etc., remains behind, as this is sucked into the measuring-tube with the liquid; in the analysis of pyroxylin it is, however, better to wait till it has completely dissolved in the beaker-funnel; when this is the case, the test is finished at once, since on standing too long time too high values are found.[1]

Nitrates and *esters of nitric acid*, such as nitroglycerine and nitrocellulose, can be analysed in the nitrometer shown in Fig. 136, but a high degree of accuracy is not obtainable therewith, since no more than 40 c.c. of gas can be measured therein. But an accuracy of 0·1 per cent., which is not surpassed by that of any other method, can be attained by means of the "nitrometer for saltpetre," shown in Fig. 139. In this a larger space for gas is provided without making the apparatus inconveniently long, by means of a bulb of nearly 100 c.c. capacity, below which the graduations extend from 100 to 130 c.c.

In Fig. 140 a nitrometer is shown which may be used for determinations, both when a large and when a small volume of gas is evolved. As it cannot be made so short as the forms shown in Figs. 136 and 139, it is not so suitable for shaking,

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[1] Newfield and Marx (*J. Amer. Chem. Soc.*, 1906, p. 877) found too low values when nitrometrically testing explosives containing paraffin, camphor, resins or vaseline, and too high results with those containing sulphur or carbonates.

but it is well adapted for use in conjunction with a "decomposition bottle" or as a "gas-volumeter" (see below).

Modified forms of the nitrometer have been described by Hempel (*Z. anal. Chem.*, 1881, p. 82), Horn (*Z. angew. Chem.*, 1892, pp. 200, 358), Pitmann (*J. Soc. Chem. Ind.*, 1900, p. 983), Dennis (his *Gas-Analysis*, 1913, p. 393).

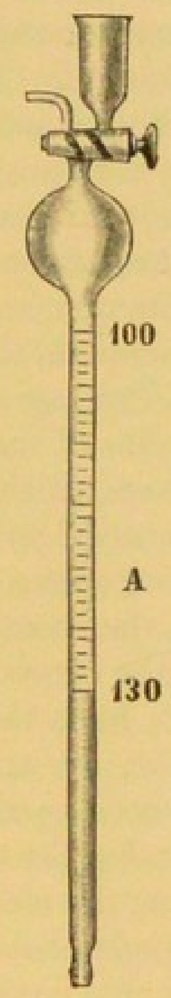

FIG. 139.

FIG. 140.

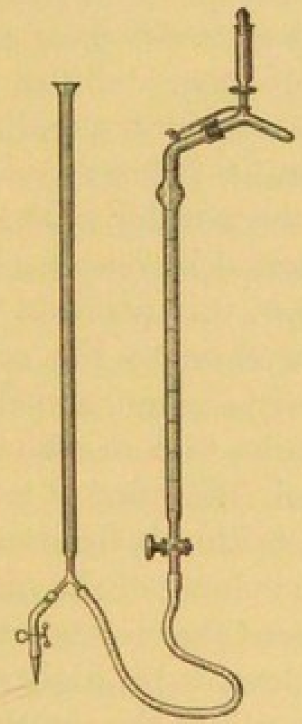

FIG. 141.

Sometimes in nitrometric analyses a somewhat considerable proportion of substances insoluble in sulphuric acid are secreted which stop up the tap. For such cases the *nitrometer of Lubarsch*, shown in Fig. 143, has been found useful. The gas-measuring tube in this apparatus is at the top bent sideways in an angle of 120° for a length of 5 cm. Immediately above the bulb is a zero mark, and the division is carried down nearly to the tap closing the tube at the bottom. Into the upper lateral tube a bent glass tube, the "receiver" 10 cm. long, 12 mm. wide, is tightly ground in. The other end of the receiver is closed; at the outer side of the bend a funnel is fused on, which is closed at the bottom by a tap, at the top by a glass stopper. The level-tube at its bottom is fitted with a branch, closed by a rubber tube and pinchcock, for running off the mercury. Both the measuring-tube and the receiver must be well dried before every test; the ground joints and the glass tap must be lubricated with concentrated sulphuric acid.

The weighed, finely-powdered example is introduced into the closed part of the receiver, and this, the funnel-tap being opened, is put on to the measuring-tube, in which the mercury should stand at the zero mark. The funnel-tap is now closed, and the requisite quantity of sulphuric acid is poured into the funnel. Now the bottom tap of the measuring-tube is opened, a minus pressure is produced by running some mercury out of the level-tube, and the sulphuric acid in the funnel is sucked into the receiver, avoiding the entrance of air. The tap of the funnel-tube is now closed, and the stopper put in at the top. When the powder in the receiver has been dissolved, which may be hastened by *cautious* heating, the receiver is turned 180°, and is fixed in this position by a rubber ring, which catches a glass hook fused on to the measuring-tube. At first the receiver is cautiously shaken, and the mercury is run out of the measuring-tube at the rate at which nitric oxide enters into it, so that no essential difference of level is produced in the tube. When the decomposition is finished, fifteen minutes are allowed to elapse, and the volume of the nitric oxide is read, after causing the liquid in the two tubes to assume the level position, keeping the mercury in the level-tube higher than that in the measuring-tube, by one-seventh of the depth of the layer of sulphuric acid, standing above the mercury in the latter (cf. *suprà*, p. 376). The volume of the receiver up to the zero mark of the measuring-tube must be known (it is marked on the receiver) and allowed for. Since the oxygen of the air present in the receiver before the experiment has been consumed by being transferred to the mercury, the cubic centimetres of the receiver-volume are multiplied by 0·209, and the product added to the cubic centimetres of NO read off. To allow for the absorption of NO in the concentrated sulphuric acid, 0·035 c.c. per each cubic centimetre of acid is added, and the result of the test calculated in the same way as for Lunge's nitrometer (p. 377).

Lunge (*Chem. Ind.*, 1886, p. 273) points out that this method gives wrong results, if the substance tested contains carbonates or other substances yielding carbon dioxide.

Nitrometer provided with a Separate Decomposing-bottle.—When compounds of nitric or nitrous acid are decomposed by shaking in the measuring-tube itself with mercury and sulphuric acid, a layer of sulphuric acid finally remains between the gas and the mercury, which has to be allowed for in adjusting the pressure for the final measurement, as stated above (p. 376). This as a rule causes no special difficulty, but when considerable quantities of substance are decomposed, much frothing sometimes occurs; on dilution with water, which is unavoidable in some cases, mercurous sulphate is precipitated, and in the analysis of dynamite the kieselguhr floats on the top of the acid, etc. These factors make the final adjustment and measurement uncertain and inexact. In such cases, for instance in the analysis of saltpetre and of explosives, it is therefore advisable to use a separate decomposition vessel, with an attached pressure-tube, as in the gas-volumeter. The gas is then always measured over a sharp mercurial meniscus, and its volume can be read with the greatest accuracy. This apparatus has been already shown, in connection with the gas-volumeter, *suprà*, p. 23, Fig. 16, where the vessel E serves for decomposing the nitrous vitriol, etc., whereupon the nitric oxide generated is driven over into the burette A, by raising the level-tube F and lowering the level-tube C.

The following Figs. 142 and 143 show the combination of a nitrometer with a special decomposition bottle more clearly.

The manipulation is then identical with that of the azotometer (*suprà*, p. 370). The substance to be decomposed is put in the outer annular space, and the decomposing agent in the inner vessel, which is fused on to the bottom of the bottle. After replacing the stopper, the bottle is connected with the tap *o* of the nitrometer; the measuring-tube A of which has been completely fillled with mercury; the stopper of the bottle is again loosened, to make sure that there is no excess of pressure in the decomposition bottle, and the latter tilted, so that the liquid in the inner vessel flows into the surrounding space. In doing this, care must be taken that the bottle is not warmed by the hand of the operator, and this applies also to the subsequent shaking, to promote the disengagement of the gas; it is safest, especially if heat is evolved by the reaction, as in decompositions by the sodium hypobromite method, to place the decomposition bottle up to the neck in a beaker filled with water, before and after the reaction. As the mercury in the measuring-tube A is depressed by the evolved gas, the level-tube C is lowered accordingly, to prevent the pressure from becoming too high; it is sometimes advisable to lower the level-tube considerably towards the end of the reaction, in order to facilitate the removal of the gas. After the original temperature has been attained, the mercury is brought to the same level in both tubes, and

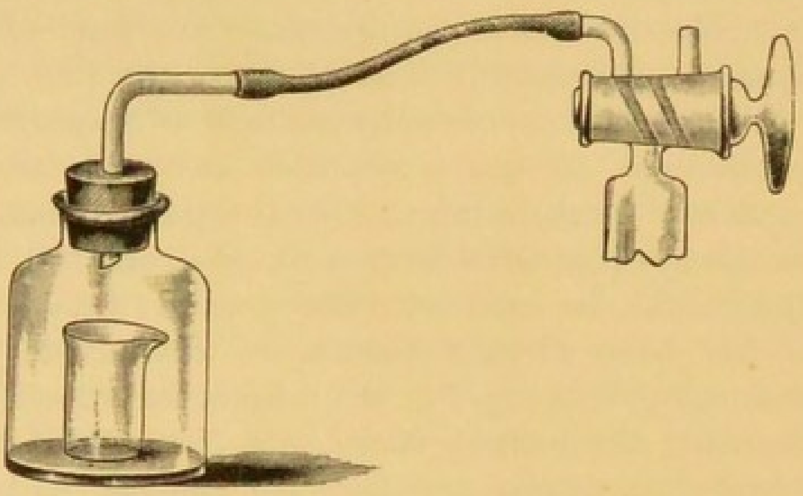

FIG. 142.

the volume of the gas read, together with the temperature and barometric pressure, as described on p. 277.

In reducing to 760 mm. pressure, it must be borne in mind that, whilst in the nitrometric operations properly so called, as in testing nitrous vitriol, nitrates, etc., the nitric oxide evolved is dry, the gas as evolved from dilute solutions is moist, and the tension of the aqueous vapour may be in these cases considered to be equal to that of pure water of the same temperature.

The reduction of the volume of gas to the normal volume (at 0° and 760 mm.) is most easily done by the tables calculated by Lunge, and reprinted in Lunge-Keane's *Technical Methods of Chemical Analysis*, vol. i., Nos. vi. to viii., pp. 921 *et seq.;* and in Lunge's *Technical Chemist's Handbook*, table No. xx. The calculation can also be performed by reversing the formula given on p. 24.

The easiest way of performing that reduction is that of employing an apparatus for the *mechanical reduction* of the volume of gases to the normal state, without observing the thermometer and barometer, as described *suprà*, pp. 19 *et seq.*, particularly by the *gas-volumeter* described on pp. 21 *et seq.* This

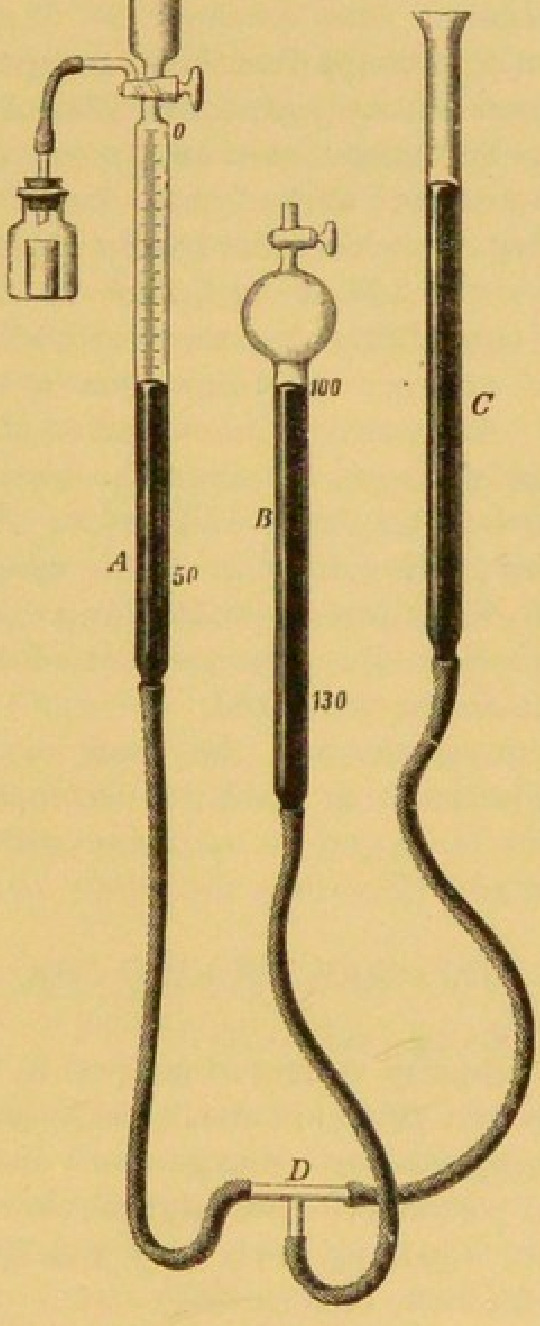

FIG. 143.

applies also to the apparatus shown in Fig. 142, where the bulb-tube B serves for the mechanical reduction just mentioned.

Lunge's *Technical Chemist's Handbook* (p. 17) contains a table for converting the cubic centimetres read off in gas-volumetric analysis into milligrammes of the substance required; also Lunge-Keane, vol. i. p. 146).

Borchers (Ger. P. 259044) describes a compensating arrangement for gas-volumetric analysis (*Chem. Zeit. Rep.*, 1913, p. 257).

Applications.—The nitrometer or gas-volumeter, combined with a "decomposition bottle," has found very numerous applications, many of which have been described by Lunge (*Chem. Ind.*, 1885, pp. 161 *et seq.*), such as the estimation of carbon dioxide (preferably by the method of Lunge and Marchlewski), of nitrogen in ammonium salts by the hypobromite method; the same in urea and in diazo-compounds; the control of the strength of acids by liberation of carbon dioxide from carbonates, the valuation of zinc dust by the hydrogen evolved; altogether in most cases where a gas insoluble in the decomposing liquid, and not acting upon mercury is given off, by the measurement of which the decomposed constituent can be estimated.

Particularly numerous are the uses for the methods in which hydrogen peroxide is used for decomposing substances, by giving up its hydrogen to combine with the oxygen of those substances, and liberating the whole of its own oxygen:

$$XO + H_2O_2 = X + H_2O + O_2.$$

This elegant and rapidly executed method is, for instance, used for testing hydrogen peroxide itself, potassium permanganate solution, bleaching-powder, manganese dioxide, potassium ferricyanide, lead peroxide, iodine solution, chromates (Baumann, *Z. angew. Chem.*, 1891, pp. 135, 198, 339, 392), nitrous acid (Riegler, *Z. anal. Chem.*, 1897, p. 665).

We must leave the special description of these methods, which do not belong to gas-analysis, to the general treatises on general and technical analysis.

The nitrometer can also be used as an absorptiometer (Lunge, *loc. cit.*) for most gas-analytical work (*ibid.*); for the collection and analysis of gases dissolved in water (*ibid.*, and

Z. anal. Chem., 1886, p. 309); for the determination of vapour densities (Lunge and Neuberg, *Ber.*, 1891, p. 729).

A modification of the Lunge gas-volumeter, in which all the connections are made of glass, has been described by Gruskiewicz (*Z. anal. Chem.*, 1904, p. 85).

Special forms of the Gas-volumeter have been designed by Lunge (*Ber.* 1890, p. 446) for the determination of nitrogen in elementary organic analysis, and by Lunge and Neuberg (*ibid.*, 1891, p. 729) for the determination of vapour densities.

Lunge (*Z. angew. Chem.*, 1892, p. 578) has devised a very convenient mechanical stand for the manipulation of the gas-volumeter (shown in Lunge-Keane's book, vol. i. p. 154), which is supplied by C. Desaga, Heidelberg, by the name of "Universal Gas-volumeter."

For the determination of carbon dioxide in carbonates, special forms of this instrument are described by Lunge and Marchlewski (*Z. angew. Chem.*, 1891, pp. 229 and 412; 1893, p. 395; *J. Soc. Chem. Ind.*, 1891, p. 658), and by Lunge and Rittener (*Z. angew. Chem.*, 1906, p. 1849); for the estimation of carbon in iron and steel, and of carbon dioxide in aqueous solutions by Lunge and Marchlewski (*Stahl u. Eisen.*, 1891, p. 666; 1893, p. 655; 1894, p. 624; *Z. angew. Chem.*, 1891, p. 412). These are described in Lunge-Keane's *Technical Methods*, vol. i. pp. 149 *et seq.*

ARRANGEMENT AND FITTINGS OF A LABORATORY FOR GAS-ANALYSIS

A person who has to carry out gas-analysis for technical purposes has in many cases to work in anything but a properly fitted-up laboratory. He may be compelled, not merely to take samples of gases in the most various places—at furnaces, flues and chimneys, in open yards, in the field, or below ground—but he must sometimes perform the analysis in the same places. Evidently under such unfavourable circumstances the accuracy of the results may be seriously impaired, but this cannot be avoided.

It is different when the analyses are made in a real laboratory. Here all arrangements can and must be provided which make it possible to work quickly and conveniently as well as accurately.

The laboratory ought to be a room exposed as little as possible to variations of temperature. The windows should give a good light, but should, if possible, be turned towards the north. The heating apparatus for use during the cold season should be arranged so that the whole room is as nearly as possible at the same temperature. The apparatus, reagents, and the water used should be kept in the laboratory itself, so as to be at the same temperature.

APPENDIX

I. *Atomic Weights, fixed by the International Committee for* 1914.

Aluminium	Al	27·1	Neodymium	Nd	144·3
Antimony	Sb	120·2	Neon	Ne	20·2
Argon	A	39·88	Nickel	Ni	58·68
Arsenic	As	74·96	Niton (radium emanation)	Nt	222·4
Barium	Ba	137·37	Nitrogen	N	14·01
Bismuth	Bi	208·0	Osmium	Os	190·9
Boron	B	11·0	Oxygen	O	16·00
Bromine	Br	79·92	Palladium	Pd	106·7
Cadmium	Cd	112·40	Phosphorus	P	31·04
Cæsium	Cs	132·81	Platinum	Pt	195·2
Calcium	Ca	40·07	Potassium	K	39·10
Carbon	C	12·00	Praseodymium	Pr	140·6
Cerium	Ce	140·25	Radium	Ra	226·4
Chlorine	Cl	35·46	Rhodium	Rh	102·9
Chromium	Cr	52·0	Rubidium	Rb	85·45
Cobalt	Co	58·97	Ruthenium	Ru	101·7
Columbium (Niobium)	Cb	93·5	Samarium	Sa	150·4
Copper	Cu	63·57	Scandium	Sc	44·1
Dysprosium	Dy	162·5	Selenium	Se	79·2
Erbium	Er	167·7	Silicon	Si	28·3
Europium	Eu	152·0	Silver	Ag	107·88
Fluorine	F	19·0	Sodium	Na	23·00
Gadolinium	Gd	157·3	Strontium	Sr	87·63
Gallium	Ga	69·9	Sulphur	S	32·07
Germanium	Ge	72·5	Tantalum	T	181·5
Glucinum	Gl	9·1	Tellurium	Te	127·5
Gold	Au	197·2	Terbium	Tb	159·2
Helium	He	3·99	Thallium	Tl	204·0
Holmium	Ho	163·5	Thorium	Th	232·4
Hydrogen	H	1·008	Thulium	Tu	168·5
Indium	In	114·8	Tin	Sn	119·0
Iodine	I	126·92	Titanium	Ti	48·1
Iridium	Ir	193·1	Tungsten	W	184·0
Iron	Fe	55·84	Uranium	U	238·5
Krypton	Kr	82·92	Vanadium	V	51·0
Lanthanum	La	139·0	Xenon	Xe	130·2
Lead	Pb	207·10	Ytterbium (Neoytterbium)	Yb	172·0
Lithium	Li	6·94	Yttrium	Yt	89·0
Lutecium	Lu	174·0	Zinc	Zn	65·37
Magnesium	Mg	24·32	Zirconium	Zr	90·6
Manganese	Mn	54·93			
Mercury	Hg	200·6			
Molybdenum	Mo	96·0			

II. *Theoretical and Calculated Density of Gases and Litre Weights at 0° C. and 760 mm. Pressure.*

One gram-molecule of a perfect gas = 22·412 litres. One litre of a perfect gas = 0·04462 × its molecular weight. Density of gases, referred to atmospheric air as unity $= \dfrac{\text{molecular weight}}{28\cdot945} = 0\cdot03455 \times \text{molecular weight}$.

	Formula.	Molecular weight.	Weight of 1 litre in grams.		Density, air = 1.		Observer.	Molecular volume, calculated from the observed density, in cubic centimetres.
			Calculated.	Observed.	Calculated.	Observed.		
Air (atmospheric)	...	...	1·2928	...	1·0000	...	...	...
Acetylene	C_2H_2	26·02	1·1610	1·189	0·8989	0·9056	Leduc	21,889
Ammonia	NH_3	17·03	0·7606	0·7708	0·5883	0·5962	Guye	22,094
Bromine	Br_2	159·87	7·1388	7·1418	0·5220	5·5243 (at 228°)	Jahn	...
Carbon dioxide	CO_2	44·00	1·9651	1·9768	1·5201	1·52908	Guye	22,258
,, monoxide	CO	28·00	1·2505	1·2503	0·9673	0·96716	Rayleigh	22,395
Chlorine	Cl_2	70·92	3·1674	3·2191	2·4501	2·491	Treadwell	22,032
Ethylene	C_2H_4	28·03	1·2519	1·2737	0·9683	0·9852	Saussure	22,007
Hydrogen	H_2	2·02	0·0900	0·08987	0·06965	0·06952	Morley	22,433
,, chloride	HCl	36·47	1·6289	1·6394	1·2599	1·2681	Scheuer	22,246
,, sulphide	H_2S	34·09	1·5226	1·5392	1·1777	1·1906	Baume, Perrot	22,148
Methane	CH_4	16·03	0·7159	0·7168	0·5538	0·5545	,, ,,	22,363
Nitric oxide	NO	30·01	1·3403	1·3402	1·0368	1·0367	Guye	22,393
Nitrogen	N_2	28·02	1·2514	1·2505	0·9680	0·96727	Rayleigh, Leduc	22,407
,, protoxide	N_2O	44·02	1·9660	1·9777	1·5208	1·5298	Guye	22,258
,, peroxide	NO_2	46·01	2·0549	...	1·5895	...	...	...
	N_2O_4	92·02	4·1098	...	3·1790	...	...	...
Oxygen	O_2	32·00	1·4292	1·4292	1·1055	1·1055	Guye	22,390
Sulphur	S_2	64·12	2·8610	...	2·2130	...	...	...
,, dioxide	SO_2	64·07	2·8615	2·9266	2·2134	2·2638	Jacquard, Pinza	21,892
,, trioxide	SO_3	80·06	3·5722	...	2·7631	...	...	...
Water	H_2O	18·02	0·8040	...	0·6219	...	...	...

III. *Changes of Volume when Gases are burnt in Oxygen.*

Name of gas.	Formula.	Combustion				Volume of gas.			Contraction.			
		requires		yields								
		Combustible gas.	Oxygen.	Aqueous vapour (condensed).	Carbon dioxide.	Before combustion.	After combustion.	After combustion and absorption of carbon dioxide.	After combustion.	Ratio of combustible gas to contraction.	After combustion and absorption of CO_2.	Ratio of combustible gas to contraction.
		Vols.	Vols.	Vols.	Vols.	Vols.	Vols.	Vols.	Vols.		Vols.	
Acetylene . .	C_2H_2	2	5	2	4	7	4	0	3	$\frac{2}{3}$	7	$\frac{2}{7}$
Benzene . .	C_6H_6	2	15	6	12	17	12	0	5	$\frac{2}{5}$	17	$\frac{2}{17}$
Butane . . .	C_4H_{10}	2	13	10	8	15	8	0	7	$\frac{2}{7}$	15	$\frac{2}{15}$
Butylene . .	C_4H_8	2	12	8	8	14	8	0	6	$\frac{1}{3}$	14	$\frac{1}{7}$
Carbon monoxide.	CO	2	1	...	2	3	2	0	1	2	3	$\frac{2}{3}$
Ethane . . .	C_2H_6	2	7	6	4	9	4	0	5	$\frac{2}{5}$	9	$\frac{2}{9}$
Ethylene . .	C_2H_4	2	6	4	4	8	4	0	4	$\frac{1}{2}$	8	$\frac{1}{4}$
Hydrogen . .	H_2	2	1	2	...	3	0	...	3	$\frac{2}{3}$	...	...
Methane . .	CH_4	2	4	4	2	6	2	6	4	$\frac{1}{2}$	6	$\frac{1}{3}$
Propane . .	C_3H_8	2	10	8	6	12	6	0	6	$\frac{1}{3}$	12	$\frac{1}{6}$
Propylene . .	C_3H_6	2	9	6	6	11	6	0	5	$\frac{2}{5}$	11	$\frac{2}{11}$

IV. *Combustion of Gases and Gaseous Mixtures* (" *Hütte* ").

	Carbon monoxide, CO.	Hydrogen, H_2.	Methane, CH_4.	Ethylene, C_2H_4.	Acetylene, C_2H_2.	Illuminating gas.	Water-gas.	Dowson gas.	Producer gas.
Molecular weight	28	2	16	28	26	12·58	15·66	24·25	28·40
Density (air = 1)	0·967	0·0695	0·555	0·985	0·906	0·434	0·54	0·84	0·98
Weight of 1 cb.m. at 0° C. and 760 mm. pressure, in kilograms	1·250	0·09	0·717	1·274	1·189	0·56	0·70	1·08	1·27
Required for burning 1 cb.m. Oxygen	0·5	0·5	2	3	2·5	1·10	0·45	0·21	0·15
Required for burning 1 cb.m. Air	2·38	2·38	9·52	14·29	11·9	5·21	2·15	1·00	0·70
Diminution of volume for 1 cb.m. gas	0·5	0·5	0	0	0·5	0·28	0·45	0·21	0·145
H_2O formed per 1 cb.m. gas, kilograms	0	0·80	1·61	1·61	0·80	1·00	0·40	0·145	0·02
Upper heating value, calories per 1 kg.	2,440	34,200	13,240	11,880	11,920	10,000	3 930	1,190	720
Upper heating value, calories " 1 cb.m.	3,030	3,080	9,470	14,990	17,070	5,600	2,750	1,285	910
Lower heating value, calories per 1 kg.	2,440	28,800	11,910	11,120	11,500	8,900	3,580	1,110	710
Lower heating value, calories " 1 cb.m.	3,030	2,595	8,505	14,020	13,580	5,000	2,500	1,200	900
Lower heating value per 1 cb.m. combustible mixture, calories	900	770	810	920	1,050	805	795	600	530

V. *Standard Solutions for Technical Gas-Analysis.*

1 vol. gas at 760 mm. and 0°, in the dry state.	Formula.	Indicated by 1 vol. of a solution containing per litre.	
		Grams.	
Ammonia	NH_3	2·1807 Sulphuric acid	H_2SO_4
"	"	2·5075 Potassium hydroxide	KOH
Carbon monoxide	CO	5·6296 Oxalic acid, crystal.	$C_2H_2O_4, 2H_2O$
"	"	14·0943 Barium hydroxide, crystal	$Ba(OH)_2, 8H_2O$
Carbon dioxide	CO_2	5·6296 Oxalic acid, crystal.	$C_2H_2O_4, 2H_2O$
"	"	14·0943 Barium hydroxide, crystal	$Ba(OH)_2, 8H_2O$
Chlorine	Cl	4·4216 Arsenic trioxide, dissolved in sodium bicarbonate	As_2O_3
"	"	11·3353 Iodine, dissolved in potassium iodide	I
Hydrogen chloride	HCl	4·8215 Silver, dissolved in nitric acid	Ag
"	"	3·4028 Ammonium sulphocyanide	CNS, NH_4
"	"	2·5075 Potassium hydroxide	KOH
Methane	CH_4	5·6296 Oxalic acid, crystal.	$C_2H_2O_4, 2H_2O$
"	"	14·0943 Barium hydroxide, crystal	$Ba(OH)_2, 8H_2O$
Nitrogen trioxide	N_2O_3	5·6230 Potassium permanganate	$KMnO_4$
Nitric oxide	NO	4·2406 Potassium permanganate	"
Sulphur dioxide	SO_2	11·3353 Iodine, dissolved in potassium iodide	I
"	"	5·0166 Potassium hydroxide	KOH

ADDENDA

Page 14. *A gas-sampling apparatus* has been described by A. E. Carr in his B. P. of 16th March 1912 and Ger. P. 270351.

Another by F. Hoffmann, La Roche & Co., in Ger. P. 272875, which automatically takes samples in rotation from various places, in connection with a measuring and checking apparatus.

Page 16. *Vessels for carrying gas samples.* According to Murmann (*Chem. Zentralb.*, 1914, i. 1722) such vessels ought not to be made of zinc, whereby carbon dioxide is absorbed, but of sheet brass.

Page 110. *A Gas-analytical apparatus* in which the capillaries are fused to the absorbing vessels, in order to avoid india-rubber joints, is described by Wempe in *Z. angew. Chem.*, 1914, i. 271.

Another apparatus, in which a measured quantity of a liquid reagent is treated with constantly new quantities of the gas to be examined until the reagent is saturated, is described by Heinemann in his Ger. P. 273726.

Billings (Amer. P. 1089390) describes an Orsat apparatus with a sample-collecting attachment controlled by clockwork, which regulates automatically the time during which the sample of gas is taken.

Page 187. *The registering gas-balance* for the continuous indication of the specific gravity of gases in motion, constructed by Simmance and Abady, and mentioned on page 187, is very favourably reported on by Friedrich Lux, in *Gasbeleucht.*, 1914, pages 416 *et seq.*

Page 241. *Estimation of Carbon monoxide.* Sinnatt and Cramer (*Analyst*, 1914, p. 217) recommend the iodine pentoxide method for which they give detailed prescriptions.

Moser and Schmid (*Z. anal. Chem.*, 1914, p. 217) convert the carbon monoxide into dioxide by passing it through precipitated mercuric oxide, and estimating the CO_2 formed by absorbing it in *N*/4 barium hydroxide solution and retitrating the excess of the latter.

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