Handbook of technical gas-analysis : containing concise instructions for carrying out gas-analytical methods of proved utility / by Clemens Winkler ; translated, with a few additions, by George Lunge.

Contributors

Winkler, Clemens 1838-1904.
Lunge, Georg, 1839-1923.

Publication/Creation
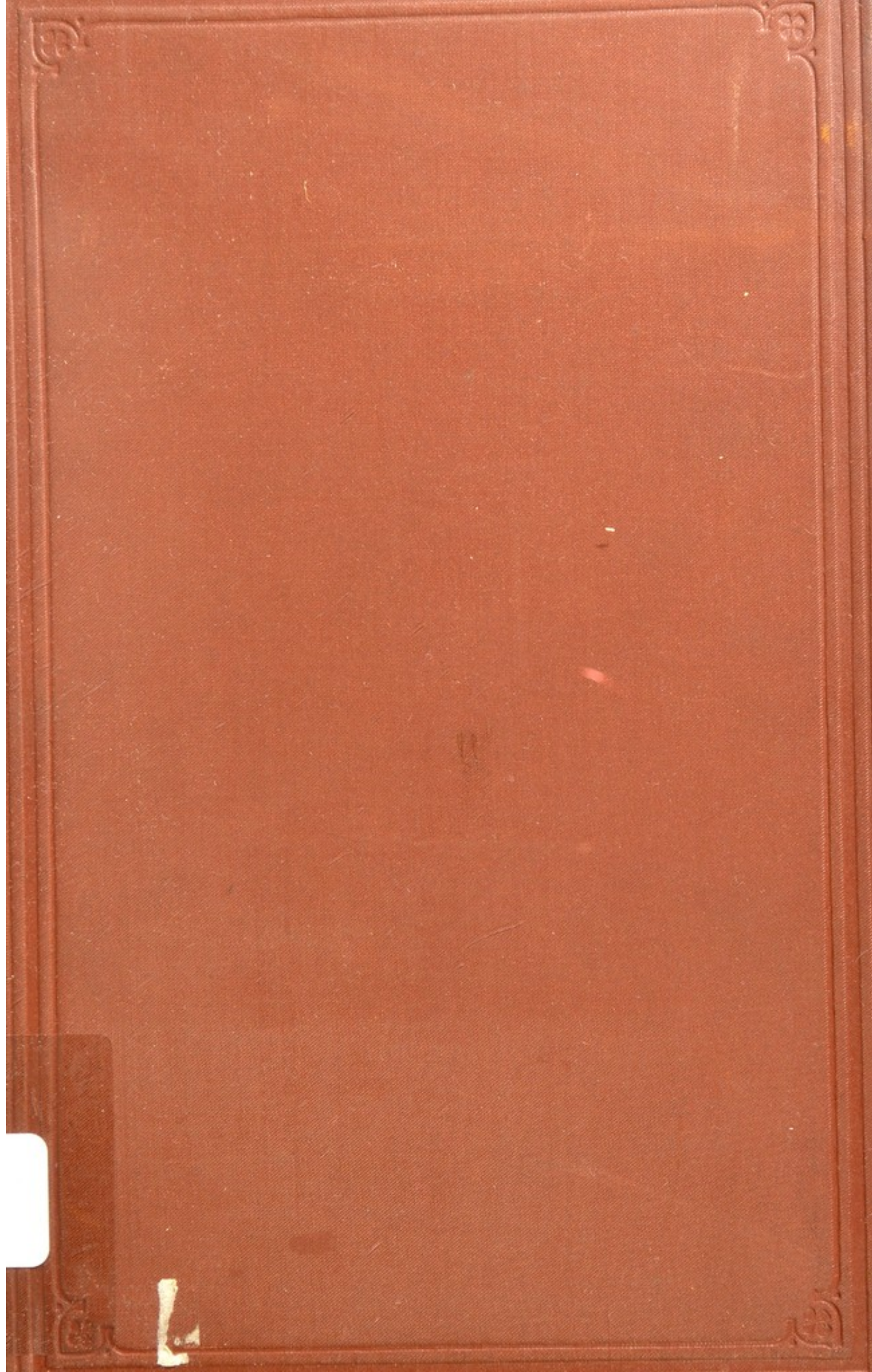
London : J. Van Voorst, 1885.

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Nov. 27th 1885

HANDBOOK

OF

TECHNICAL GAS-ANALYSIS,

CONTAINING

CONCISE INSTRUCTIONS

FOR CARRYING OUT

GAS-ANALYTICAL METHODS OF PROVED UTILITY.

BY

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TRANSLATED, WITH A FEW ADDITIONS,

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comprehend and manage any other gas-analytical process or apparatus he may meet with or require for his special purpose. The scope of this book does not in any way embrace the methods of gas-analysis practised for purely scientific purposes, for instance, all those in which mercury is employed for confining the gases; but it will, for all that, have great interest for scientific chemists.

The selection which the Author has made from the large mass of material now accumulated, was evidently, to a certain extent, dictated by special circumstances. German sources were mainly used by him, as these far more than sufficed for the purpose which he had in view—that of furnishing a sufficient number of illustrations for all parts of his field. The Translator has been under a strong temptation to supplement the book by some other examples of apparatus; but this proved unmanageable, as the present treatise would thus have lost its character, as indicated above, and as then, with greater pretensions, it might perhaps have been more open than it is at present to the objection that the treatment of the subject was not sufficiently exhaustive. The Translator has therefore contented himself with adding a few notes where they seemed to be especially called for, and with describing two apparatus of his own construction which have been found very useful just for industrial purposes, and which seemed to supply a want. All the additions he has made are marked, the text being in other respects a faithful rendering of the German original.

The Translator must acknowledge the most valuable services of Dr. Atkinson in looking over the proofs and improving the style of the translation.

All the apparatus mentioned in this book can be supplied by Messrs. Mawson and Swan, of Newcastle-upon-Tyne, or by any other dealers in chemical apparatus.

It is hoped, then, that English chemists, gas-managers, engineers, factory inspectors, and others interested in technical gas-analysis, will receive this work with favour, and that it will be as widely employed and as useful as Winkler's works have been in his own country.

Zürich, August 1885.

AUTHOR'S PREFACE.

THE gases, those invisible products of industrial activity, have long been denied the attention which they have as much right to claim as the solid and liquid substances. Only during the last few years a change for the better has taken place in this respect; and this change dates from the time when the examination of gaseous mixtures began to develop into an independent branch of analytical Chemistry. Much is still left to be done, but at least a beginning has been made in the way in which we must proceed, lest our age might hereafter be taxed with a waste of material, unworthy of its intellectual progress. In the present day every factory of any size* is more or less provided with apparatus for gas-analysis; but the most striking proof of the spread of technical gas-analysis is furnished by the continually increasing demand for young chemists familiar with its manipulation, and by its elevation to the rank of a special study taught at various Polytechnic Schools.

Under such circumstances the issue of a handbook of technical gas-analysis must appear justified; I even cherish the hope that it will prove fruitful in more respects than one. Unlike the 'Handbook for the Chemical Investigation of Industrial Gases,' published by me and completed five years ago, which treated this subject in a far more exhaustive way and with special regard to chemical manufactures, this present treatise is intended to sketch concisely a system of teaching, by means of which it is possible to learn

* *I. e.* in Germany.—*Translator.*

the best and most approved methods of gas-analysis in a short time—a system of teaching which I have applied with complete success in the laboratory of the Royal Mining Academy for a number of years.

I have found the methods hitherto employed of estimating combustible gases either by explosion, or by burning them with the aid of wires heated by an electric current, to be unsuitable, or even untrustworthy. When employing water or aqueous solutions to confine the gases, analyses by explosion are always awkward; nor do they appear convenient, owing to the necessity of adding oxygen or detonating gas. The same inconvenience attaches to the employment of an electric current sufficient to produce a high degree of heat. On the other hand, where the results are to be really correct, the demand for a saving of time cannot be satisfied beyond a certain limit; and this must be specially said of the estimation of methane, which is burned with such difficulty.

Owing to the concise character of this book, the names of authors and quotations of authorities had to be omitted. The selection of the methods was made on the principle of not quoting anything but what I had actually tried myself.

The various Tables forming the Appendix (the last of which I owe to the kindness of Professor Leo Liebermann of Budapest), will, I trust, be found acceptable.

CLEMENS WINKLER.

Freiberg,
September 27th, 1884.

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INTRODUCTION.

GENERAL REMARKS.

THE chemical examination of gaseous mixtures, for the purpose of quantitatively estimating their constituents, is usually effected by *measuring*, not by weighing, the latter, owing to the general physical behaviour of gases : gas-analysis being a volumetric process, and hence also called *gasometry*, or *gasometric* or *gas-volumetric* analysis.

Consequently the results of gas-analyses are not usually expressed in per cent. by weight, but in *per cent. by volume.* In exceptional cases some of the gaseous constituents are estimated by weighing; but, even then, the weight is reduced to the corresponding volume from the well-known weight of a litre of the gas in question.

Since the volumes of gases are essentially influenced by moisture, pressure, and temperature, they are measured when saturated with moisture and under the existing conditions of atmospheric pressure and temperature, as observed at the time by means of the barometer and thermometer. The volume found in this way (*uncorrected volume*) is afterwards *reduced to the normal volume*; that is, from the volume actually observed it is calculated what volume the gas would occupy in a perfectly dry state at the normal barometric pressure of 760 millims. and at the normal temperature of $0°$ C. (*corrected* or *reduced volume*). This correction may be omitted if the analyses are very quickly performed or if they do not require any considerable degree of exactness.

The *analytical process* followed in the examination of gases generally consists in transforming one constituent after the other into a compound of a different state of aggregation. From the *contraction of volume* thus produced, the volume of the special constituent in question can be deduced directly or indirectly. This can be done :—

(1) *By direct absorption.*—For instance, carbon dioxide is taken up by a solution of potassium hydroxide, oxygen by moist phosphorus, carbon monoxide by a solution of cuprous chloride in hydrochloric acid. They are thus dissolved out, which causes a decrease of the volume of gas originally employed to the extent of their own volume.

(2) *By combustion.*—Hydrogen is burned with oxygen, forming water. In this process two volumes of hydrogen unite with one volume of oxygen ; both gases vanish as such, and a contraction takes place to the extent of three volumes. Hence the volume of the hydrogen originally present, is found on multiplying by $\frac{2}{3}$ the contraction of volume observed.

(3) *By combustion and subsequent absorption of the products.*— Certain gases cannot be directly absorbed, nor are they transformed by combustion into compounds condensing of their own accord, but these compounds are capable of being absorbed. Thus methane is burned into water and gaseous carbon dioxide, which is absorbed by a solution of potassium hydroxide; 1 vol. of methane and 2 vols. of oxygen (altogether$=3$ vols.) in this process yield 1 vol. of gaseous carbon dioxide. The contraction produced by absorbing the latter is $3-1=2$ vols. From this we see that the volume of the methane originally present in the gas can be found in three ways :—

(*a*) By dividing by 2 the contraction accompanying the combustion.

(*b*) By absorbing the carbon dioxide formed in combustion, whose volume is equal to that of the methane.

(*c*) By dividing by 3 the contraction of volume consequent upon the combustion and the absorption of the CO_2 formed.

Gaseous constituents which do not lose their gaseous state, either by absorption, or by combustion, or by combustion and absorption combined, are measured directly in the state of gas; that is, they form the *residue* remaining at the close of the operation of gas-analysis. This case refers only to one gas, viz. nitrogen.

In order to arrive at results which satisfy practical requirements, without laying claim to the utmost attainable degree of accuracy, *technical gas-analysis* must first and foremost aim at working by the simplest possible means and with the least possible waste of time. Scientific investigations are not tied to time and hour; but where the question is that of practically controlling the working of some technical process, it is often necessary to get quickly an idea of this from time to time; or it may be instantaneously wanted, even if that idea should be only a rough one. Analytical results, which the manager of the works can only receive from the chemist after the lapse of days or weeks, are in most cases entirely useless to him, let them be ever so accurate. This must be steadily borne in mind when working out methods of gas-analysis; and, fortunately, the progress made during the last few years has shown that, although the procedure has been simplified, the accuracy of gas-analyses has steadily increased.

For measuring the gases we employ *measuring-vessels* of suitable construction, gauged and divided according to the metrical system, within which vessels the gases are confined. As *confining-liquid* we always employ pure water whenever practicable. Mercury should be avoided as far as possible; glycerine and fatty oils, which do not offer the least advantage, but many inconveniences, must be entirely avoided. If gases very soluble in water have to be treated, they are either confined and measured between glass taps, avoiding any liquid; or the soluble part of the gases is first estimated by absorbing it by means of a chemically active solvent of known strength, and only the unabsorbed gases are subjected to volumetrical analyses. In such cases the absorbable gas is estimated by *titration*. In order to avoid any delay by unnecessary calculations, the strength of the standard solutions used for titration should be made to correspond with the volume-weight

of the absorbable gas; so that a standard solution is considered *normal*, if a certain measure of it is capable of absorbing exactly one volume of the gas in question, when corrected for pressure and temperature.

Hence the estimation of the volume of a gas can take place :—

    (*a*) By *direct measuring*;
    (*b*) By *titration*;
    (*c*) By *weighing*.

The *absorption of gases* is carried on either within the measuring-apparatus, or preferably outside the same in special absorbing vessels. *Combustions of gases* are always made outside the measuring-vessels. Care must be taken that during the analytical operations pressure and temperature suffer no essential changes; the laboratory in particular and the confining and absorbing liquids ought to have the same temperature; the influence of draughts, radiant heat, and of other external agencies which alter the volume of gases, must be excluded from the apparatus.

CHAPTER I.

ON TAKING SAMPLES OF GASES.

SAMPLES of gases may be taken in various ways according to circumstances, but it is usually done by means of an aspirator. Previously to collecting the gas, care must be taken to *remove the air completely from the connecting-tubes* and other intermediary apparatus. This can be done by interposing in the connecting-tube, immediately before its junction with the collecting-vessel, a T-shaped branch whose lateral arm is joined to a small india-rubber aspirating-pump (see below). By means of this pump it is easy to remove the air between the place whence the sample is taken and the collecting-vessel, and to fill the tubing with the gas under examination; so that, on the commencement of sampling, only the latter can get into the collecting-vessel. If the gas is under pressure, so that it issues of its own accord, the employment of an aspirating-pump is evidently unnecessary.

1. *Aspirating-tubes.*

In order to take a sample of gas from any place, such as a furnace, a flue, a chimney, &c., an *aspirating-tube* is introduced into that place in the shape of a tube open at both ends, the outside end being connected with the collecting-apparatus by means of an india-rubber tube. It is of very little use to provide the aspirating-tube with several branches, or with a slit as shown in fig. 1, with the idea of getting a better *average sample* in this manner. Although it is possible, by providing a movable cleaning-rod, to prevent any soot or dust from stopping up the slit, still such a contrivance does not ensure a thoroughly trustworthy average sample, because the rate of speed of a gaseous current passing through a flue &c. is not the same all over, and, owing to friction, is con-

siderably less in the neighbourhood of the walls. Moreover, the gas is more quickly sucked in at that end of the slit which is

Fig. 1.
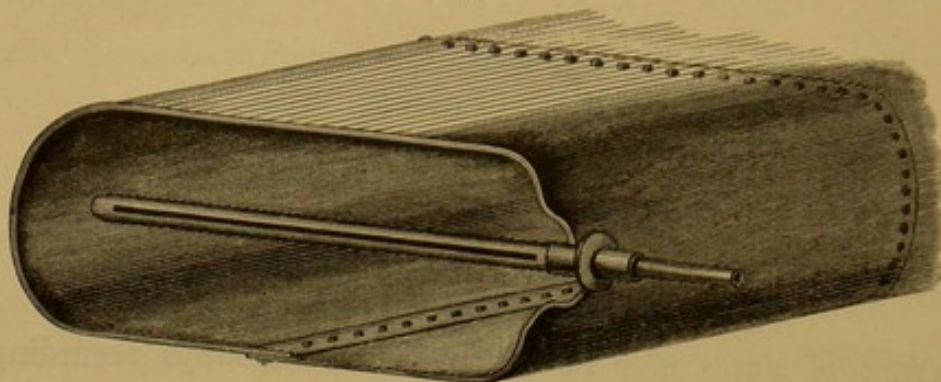
nearest to the aspirator. Up to the present we do not know of any process for taking from a moving current of gas such a sample that it may be said to represent a perfectly correct average of the whole bulk of the gas. But it is possible to come very near the truth by producing a strong *primary current* from the place

Fig. 2.
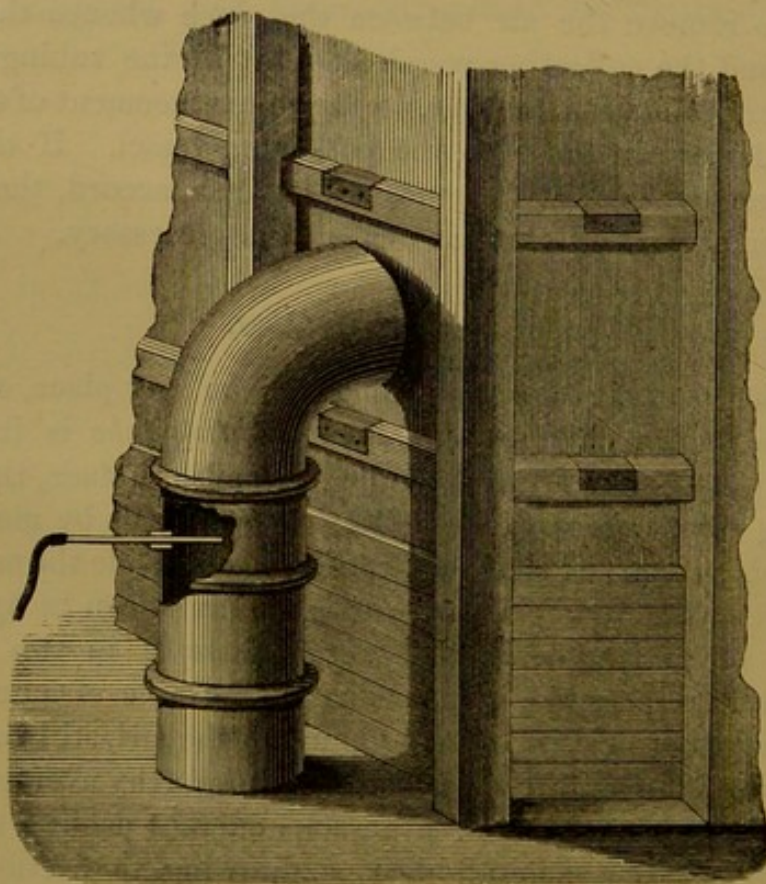
of sampling, and branching off a small *secondary current* from the former by means of a T-pipe, the latter current forming the average sample.

The material of the aspirating-tube must be calculated to resist the prevailing temperature, and not to exert any chemical action upon the gas.

Wherever it is possible *glass tubes* are employed for this purpose, because they are easily constructed, inserted, and cleaned, and because they are neither acted upon by, nor do they act upon, the gases. If the temperature admits of it, the glass tube is simply fixed by means of a perforated cork or caoutchouc stopper, for instance in sampling the gases of pyrites-burners or vitriol-chambers (fig. 2). In such cases it is usually sufficient simply to bore a hole in the lead; but if greater durability and tightness are desired, a small piece of lead-tubing may be soldered on to the hole.

A simple hole is also sufficient for providing an opportunity for introducing a cork and glass tube into the masonry of a chimney or flue. But it is preferable, especially where many samples of gas have to be taken at various times, to cement, once for all, a por-celain socket-pipe into the hole made in the masonry by means of common clay or of fire-clay, and to tightly insert the cork with the glass tube into the socket.

Porcelain aspirating-tubes are employed, if the temperature of

Fig. 3.
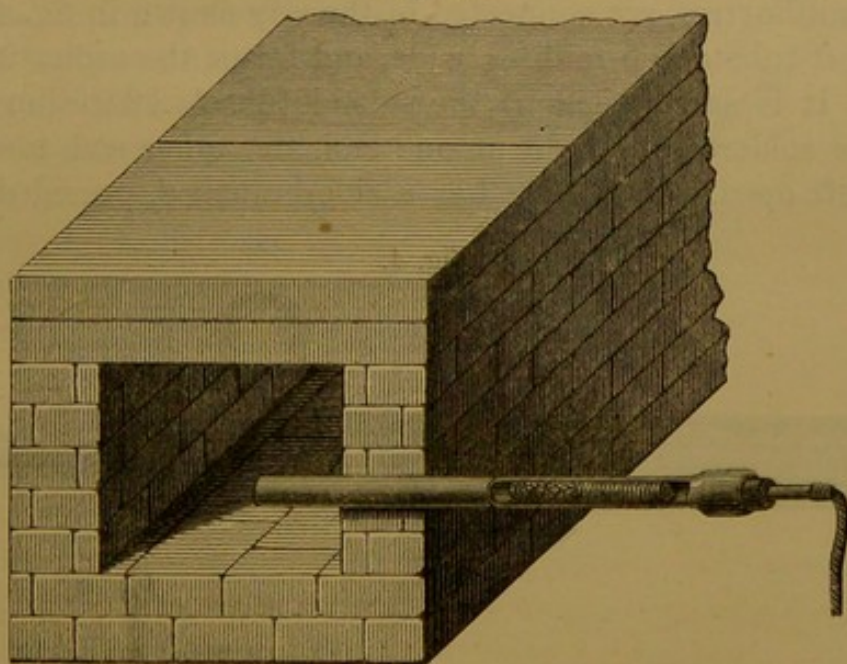
the place where the gas is to be sampled is high enough to soften glass. The porcelain tube should be so long that it projects a good deal beyond the outside of the masonry; in case of need the projecting part may be filled with a narrow-mesh wire-gauze, which usually suffices for cooling the gas passing through. If the gas is charged with soot or dust, the projecting part is filled with asbestos or glass-wool in order to retain the solid particles (fig. 3). Porcelain tubes should be gradually heated up, to prevent their cracking by the heat; unglazed earthenware pipes, which are sometimes employed in their place, are certainly less sensitive to changes of temperature, but are not gas-tight, and on this account cannot be recommended.

Aspirating-tubes made of metal (iron, brass, copper, silver, platinum) have the advantage of not being fragile, and may be employed wherever the temperature is not high enough to cause the metal to fuse, or to allow the gases to diffuse, or to exert a chemical action upon them. But an inconvenient property of metals is their great conductivity of heat. Corks inserted into them may be charred; india-rubber tubes, joined to them, generally stick fast and soften, or melt altogether. Nevertheless metallic aspirating-tubes cannot be dispensed with in many cases, and it may hence become necessary to avoid the drawbacks just mentioned by providing them with cold-water jackets. In order to cool the whole length of tubing, the following system may be adopted :—

Three copper tubes of different width, the metal of a thickness of 1 or 2 millimetres, are connected in the way shown in fig. 4. The innermost tube *a* is 5 millims. wide, and forms the aspirating tube proper; it is surrounded by the second tube *b*, 12 millims. wide, which is soldered up tight at one end, the other end towards *A* being left open. This tube has a side-branch *d*, provided with a

Fig. 4.
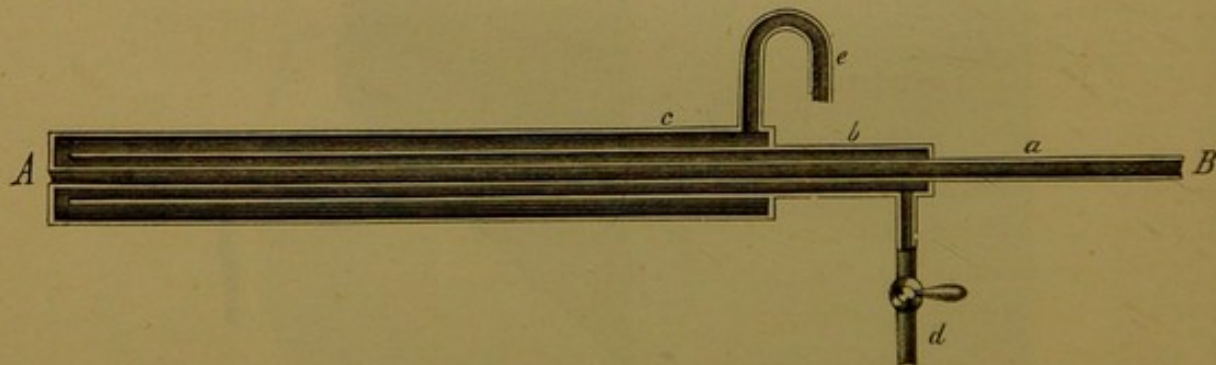
stopcock, for admitting the cooling water. The outer jacket is formed by the tube c, 20 millims. wide, which at the end A is soldered to the tube a, at the end near B to the tube b. The tube c is also provided with a branch e, through which the cooling water, which has been heated on its way through the tubes b and c, is run off again. The length of the tube A B may vary according to circumstances; usually 0·6 to 0·7 metre (about 2 feet) will suffice. The inlet and outlet for the cooling water should be made wide enough to admit of a rapid flow of water, and so prevent any formation of steam.

In order to employ this apparatus for withdrawing gases from a heated furnace, a hole is made in a suitable place in the furnace-wall, about 3 centims. (say 1¼ inch) wide. The stopcock d is connected by an india-rubber tube with a water-pipe; it is then opened, and, as soon as the water issues at e, the end A is introduced through the hole into the furnace. The joint is at once made tight by a wet mixture of fire-clay and common clay. The end a is now connected with the reservoir for the gas and the aspirator, in order to withdraw a sample of the gas. Water should be caused to flow rapidly through the tubes up to the moment when the apparatus has been taken out of the furnace.

Very hot gases should be sucked off slowly and with careful cooling, because their constituents may be in a state of *dissociation*. When examining gaseous mixtures, whose dissociation has partially become permanent in consequence of violent cooling, very erroneous conclusions may be arrived at; in such cases especially we may expect to find carbon monoxide coexisting with oxygen.

It has also been attempted to cool the gases by immediate contact with water, in the manner shown in fig. 5. The copper tube, 6 to 8 millims. wide, is U-shaped. The part E C, which is intro-

Fig. 5.
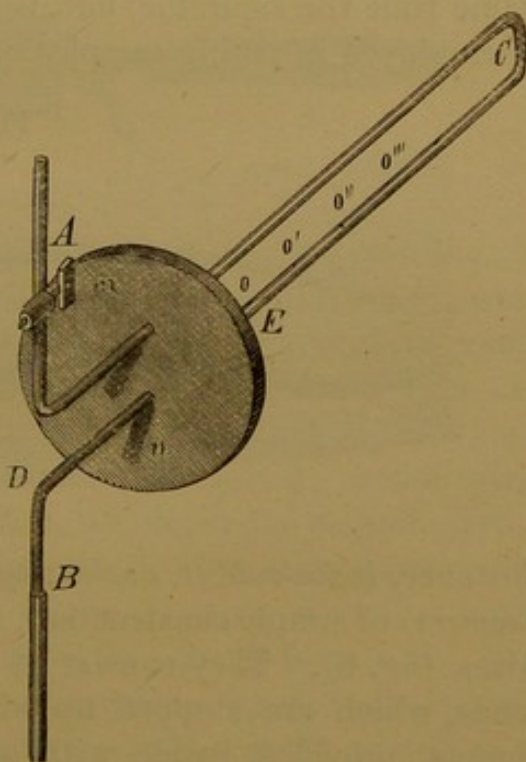
duced into the hot gas, is provided with a number of fine cuts, 0, 0', 0", 0''', made by a saw, for admitting the gas. $m\,n$ is a copper disk, by which the tube is fastened to the outside of the wall of the furnace. In order to start the apparatus the stopcock A is opened, and water is thereby admitted, which runs through the bent tube $A\,C\,B$, and is carried off by an india-rubber tube into a gas-holder filled with water, where the water and the gas carried away with it are separated. At first a little water squirts out through the saw-cuts, but soon the tube $C\,D\,B$ begins to act as a siphon, and, if the cock A is set rightly, gas is aspirated through the saw-cuts and collected in the gas-holder.

As in this process the gas is brought into intimate contact with a large quantity of water, it cannot be avoided that certain gases, *e. g.* carbon dioxide, are absorbed to a considerable extent. Hence this manner of sampling can only be employed in a restricted number of cases; but it may do good service where it is only a question of finding the relative proportions of gases possessing a slight solubility in water, such as oxygen and nitrogen.

2. *Aspirating Apparatus.*

In the last-mentioned case the conducting-tube forms at the same time the aspirator, but usually a special aspirating apparatus is employed in taking samples of gases. As such we may use, for

Fig. 6.
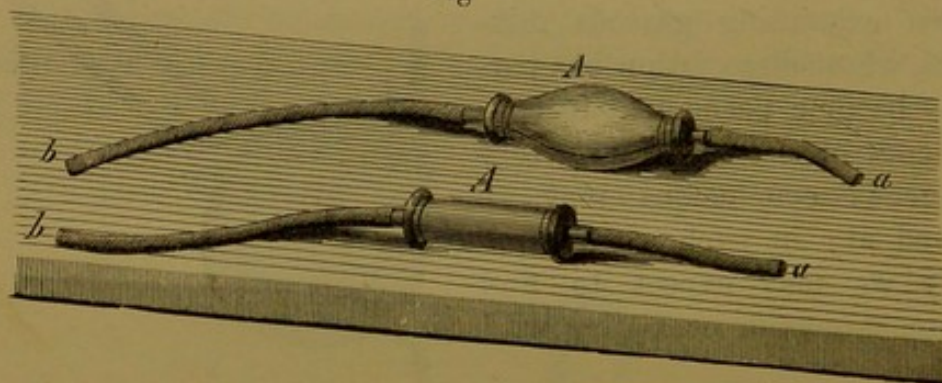
instance, *india-rubber aspirating- and force-pumps* (*hand or foot blowers*) of simple construction, as met with in commerce in various sizes (fig. 6). They consist of a stout vessel A, with cylindrical ends, which are stopped up with turned and perforated wooden bungs, provided inside with a very simple kind of valve (viz. leather clacks with a pasteboard strengthening). India-rubber

tubes of differing length are attached to these bungs; the shorter piece *a*, about 20 centims. long, forms the aspirating-tube, the longer piece *b*, about 40 centims. long, the discharging-tube. On compressing the vessel *A* by hand or by foot, its gaseous contents are forced out through *b*; when the pressure is relaxed the elastic vessel resumes its former shape, and is thereby filled with a new supply of gas through *a*. By a continued alternation of these two manipulations considerable quantities of gas may be aspirated and forced away within a short time, say 12 to 18 litres per minute, and the valves close tightly enough to overcome a pressure of several metres of water. This contrivance is extremely convenient for filling a bottle, a tube, or any vessel whatsoever, with the gas to be examined. In this case no confining (luting) liquid is required, but there must be an ample supply of the gas in question, for the air previously present can only be assumed as having been entirely replaced by the gas, provided the five-fold volume of the latter has passed through the blower.

Where high-pressure steam can be had, gases may be aspirated continually or for a great length of time by means of a *steam-jet aspirator* (fig. 7). A strong glass tube, about 3 centims. wide, or

Fig. 7.
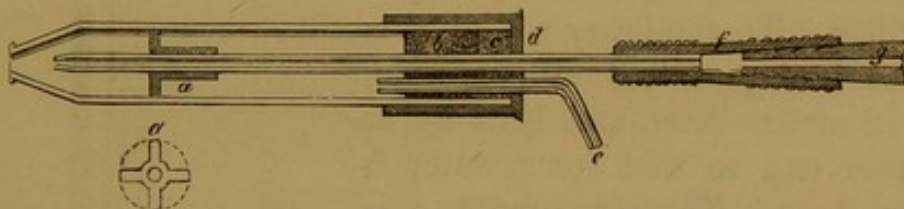
in lieu of this a metallic tube of a length of 20 to 25 centims., is drawn out at one end to an orifice of 6 millims. width; a steam-pipe is fixed in its longitudinal axis in such a way that its point, tapering to 2 millims. bore, ends about 12 millims. behind the orifice of the outer tube. Near this point the steam-pipe is kept in its place by a ferrule *a*, made of wood or metal; at the other end it is tightly fixed in the cork *b*, which, in its second perforation, carries the tube *e*, through which the gas is aspirated. This cork, to make the juncture firmer, is covered with a layer of cement *c*, and the whole is confined in a metal ferrule *d*. The aspirator should be joined to the steam-pipe *g* by an india-rubber tube with hemp lining *f*, since ordinary india-rubber tubing does not resist steam-pressure.

Apart from these "dry" aspirators, very many such are constructed with a water-luting.

It is frequently necessary to aspirate a gas continuously for a long time, whether in order to measure its volume in a gas-meter, or to take a smaller sample from it, or to absorb one of its constituents present in very small quantity. In such cases it is customary to apply that kind of aspirator in which the gas is carried away by a jet of water, and whose efficiency may be sufficient to overcome the atmospheric pressure. Very many such apparatus have been constructed, of which only a few of the best are described here.

Fig. 8.

Bunsen's water-air pump (fig. 8) consists essentially of a cylindrical glass vessel *A*, into whose contracted upper end a narrower glass tube is soldered, communicating on one side with the glass vessel *B*, and on the other side reaching nearly down to the lower contraction of *A*, where it ends in a fine orifice. To the lower end of *A* is joined a lead pipe *b*, 8 millims. wide, 10 to 12 metres long, and bent up at the lower end so that some water is retained here. The side-branch *a* is connected with a water-reservoir, or with the service-pipe; the flow of water, which need not take place under pressure, can be once for all set to a certain rate by means of a screw-clamp, and completely shut off by another. If water is run in through *a*, the lead-pipe *b* is filled with a column of water balancing the weight of the atmosphere, and the jet of water following this carries air along through *c*, in order to yield it up only at the lower end of the lead pipe. If *c* remains open, the air is continuously and strongly sucked in, so long as the flow of water is not interrupted. If, however, *c*, or a space communicating with *c*, is closed, a vacuum is produced, corre-

sponding to the Toricellian vacuum of the water-barometer formed
by the apparatus. The vessel *B* is not essential for the purpose
of aspiration; its object is principally to retain any liquid carried
along mechanically, and to admit of discharging the latter through
f from time to time. The tube *d* is connected with a mercurial
pressure-gauge, which indicates the progress of the evacuation; *e* is
the continuation of the aspirating-tube *c*, and is connected with the
space which is to be evacuated, or from which a sample of gas is
to be taken. Bunsen's pump requires no head of water, but a
considerable length of downward pipe as above mentioned; if,
however, the purpose is not that of complete evacuation, but merely
of aspirating gases, the downward tube may be shortened down to
1 metre, or even less than that. The long lead tube *b* may then
be replaced by an india-rubber tube, closed at the lower end by a
bent glass tube.
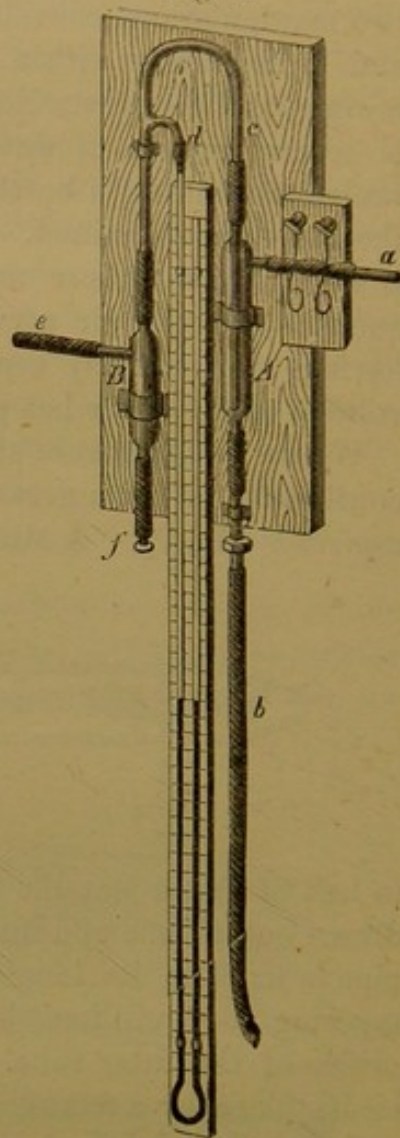
The *water-jet pumps* as constructed by Arzberger and Zul-
kowsky, H. Fischer, Körting Brothers, Th. Schorer, and others,
work well and do not require any height of fall for the waste water;
but, on the other hand, they require a head of 5 to 10 metres
of water for feeding. Their construction, which has been very
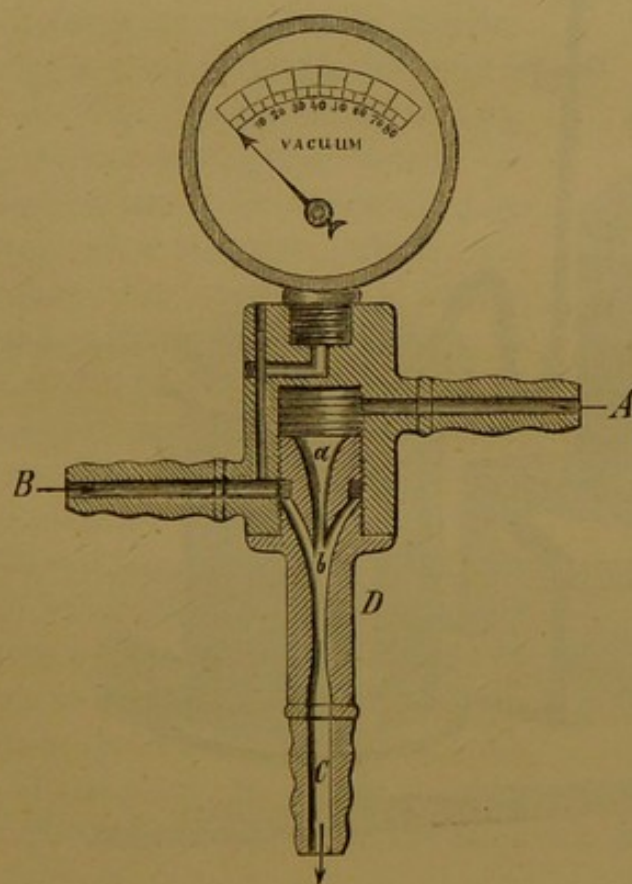
Fig. 9.   Fig. 10.

much varied, is apparent from fig. 9.   The water enters at *A*,
issues from the conical tube *a*, 1 millim. 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 with
the corresponding pipes by elastic tubing ; the neck *D* is held
in a support.   A small vacuum-meter communicating with *B* in-
dicates the degree of lessened pressure.

Finkener's aspirator (fig. 10) is on the same principle, but is
simpler and made entirely of glass.   Water enters through the
tube *a*, which is drawn out to a point ; runs through the tube *c*,
which is bell-shaped at the top, contracted in the middle, and again
widened at the bottom-end ; and aspirates air through *b*, which
forms a frothy mixture with the water issuing at *c*.

Another kind of apparatus admits of both aspirating and col-
lecting the gases, sometimes also of measuring them, or rather
that part which is not sensibly soluble in water.   In many cases
the analytical apparatus itself, such as the *gas-burette* or the gauged
collecting-bottle, is employed as an aspirator, by being filled with
water, which is made either to run off within the space containing

Fig. 11.
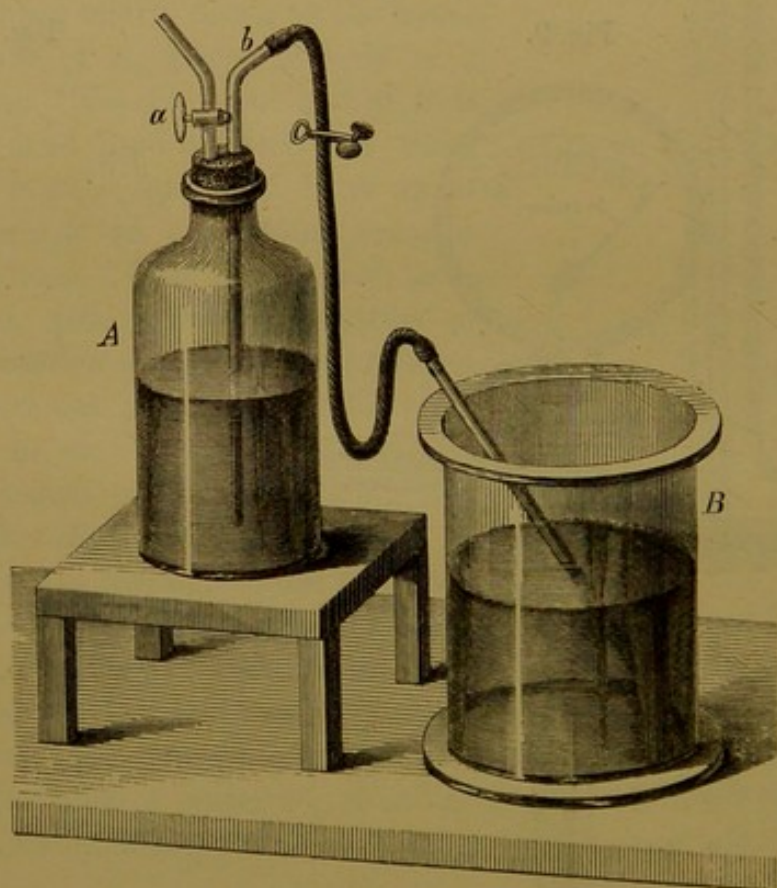
the gas to be examined or after connecting the apparatus with the aspirating-tube.

If somewhat large quantities of gases have to be collected, an *aspirating-bottle*, as represented in fig. 11, may be employed. This bottle *A* is placed on a wooden stool ; its india-rubber cork is provided with a glass stopcock *a* and a tube *b*, reaching nearly down to the bottom, and on the outside is connected by means of an elastic tube with a straight glass tube of sufficient length to act as a siphon, capable of drawing off all the water contained in the bottle. The connecting elastic tube can be closed by a screw-clamp, which also permits the outflow into the vessel *B* to be regulated. Before taking the sample the aspirating-bottle is filled with water by so altering the levels, with the aid of the siphon, that no air-bubbles remain, and the water ultimately rises to the top of the stopcock *a*. The latter is now connected with the aspirating-tube, already filled with the gas to be sampled. As soon as the stopcock *a* is opened, the siphon begins to act and the bottle is filled with gas.

Robert Muencke's double aspirator (fig. 12) is very convenient, especially where volumes of gas approximately equal have frequently to be aspirated. Two bronzed cast-iron pillars support in suitable bearings a steel spindle, to which are attached, in opposite directions, two cylindrical glass vessels of known volume, communicating by means of a stopcock, which also regulates the outflow. A simple spring arrangement, attached to the front part of the spindle or the upper part of the front pillar, serves for fixing the glass vessels in a perpendicular position. Each glass cylinder is closed with a brass plate affixed with screws, pierced by a bent glass tube reaching nearly down to the bottom of the vessel, and on the outside connected with an elbow-piece, to which the two pieces of tubing are attached which communicate with the stopcock fixed to the ground-plate.

Fig. 12.
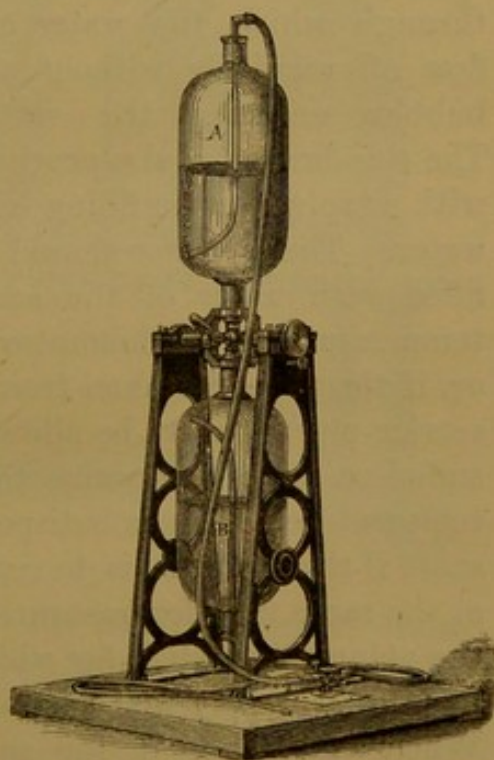
This stopcock is marked for the vessels *A* and *B*, and is bored in such a way that, if turned as in the figure, it brings the upper vessel *A* into communication with the apparatus through which gas is to be aspirated, and at the same time connects the lower vessel *B* with the atmosphere. When the upper vessel is run off, the button of the spring-arrangement is pressed, the cylinders shifted round the spindle by 180°, and the lower stopcock turned to the same extent. In this position the vessel *B* is connected with the gas apparatus and *A* with the atmosphere.

Thus this double aspirator permits of almost continuous action without any change of tubing.

A very convenient form of *zinc aspirators* is shown in fig. 13. The vessel *A*, containing 10 to 15 litres, is placed in a wooden stand; it ends at the top in a stopcock *b*, and at the bottom in a slightly tapering tube, provided with the tap *c*, and bearing a thin brass tube *d*, through which the water can flow off regularly without air-bubbles entering the vessel. The side-branch *a*, also provided with a tap, serves for filling with water. The aspirator should be filled with water of the same temperature as the laboratory; or, if the water is taken from a service-pipe, it must be allowed sufficient time to acquire that temperature. This is indispensable if the aspirator is to serve at the same time for measuring the volume aspirated, for which purpose it is very well adapted. When employing it for such measurements, the tap *b* is connected by means of an air-tight screw-socket with a glass T-

Fig. 13.
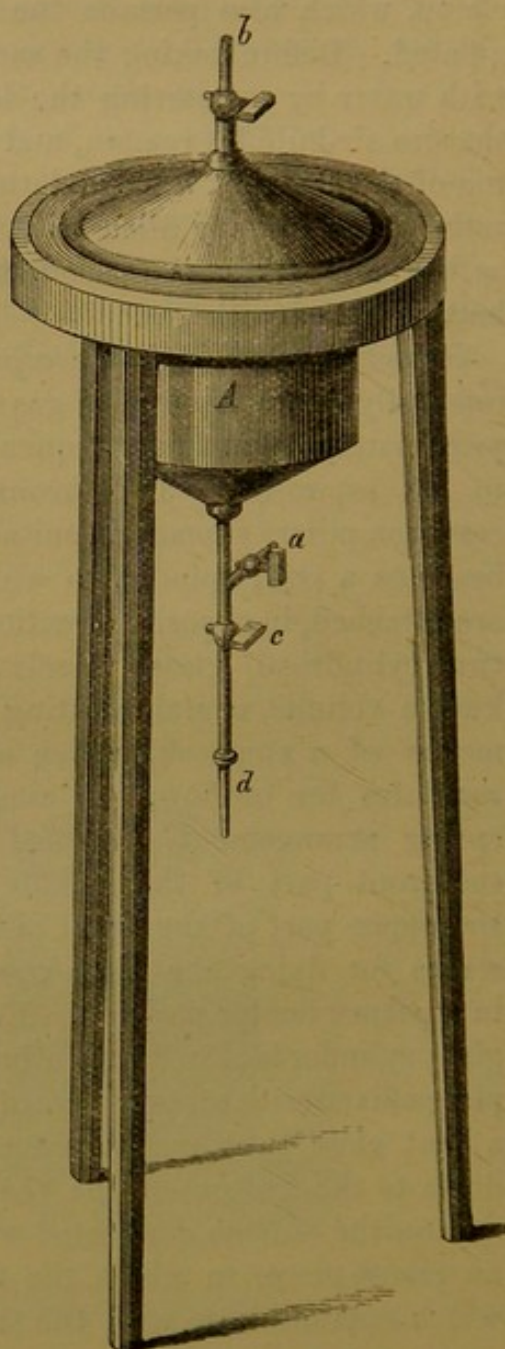
piece, the upper limb of which ends in a small mercurial pressure-gauge, whilst the side limb is connected with the aspirating-pipe. By opening the taps b and c the gas is aspirated and the water which runs off is collected in a litre-flask placed below. The moment the water in the latter has reached the mark, the tap c is closed, but b is only closed the moment the pressure-gauge has come to the level again. When this happens a volume of gas exactly equal to that of the water run off has been aspirated.

For aspirating and at the same time measuring large volumes of gas, the *automatic aspirator of J. Bonny* (patented in Germany) can be employed. The essential feature of this apparatus (fig. 14)

Fig. 14.
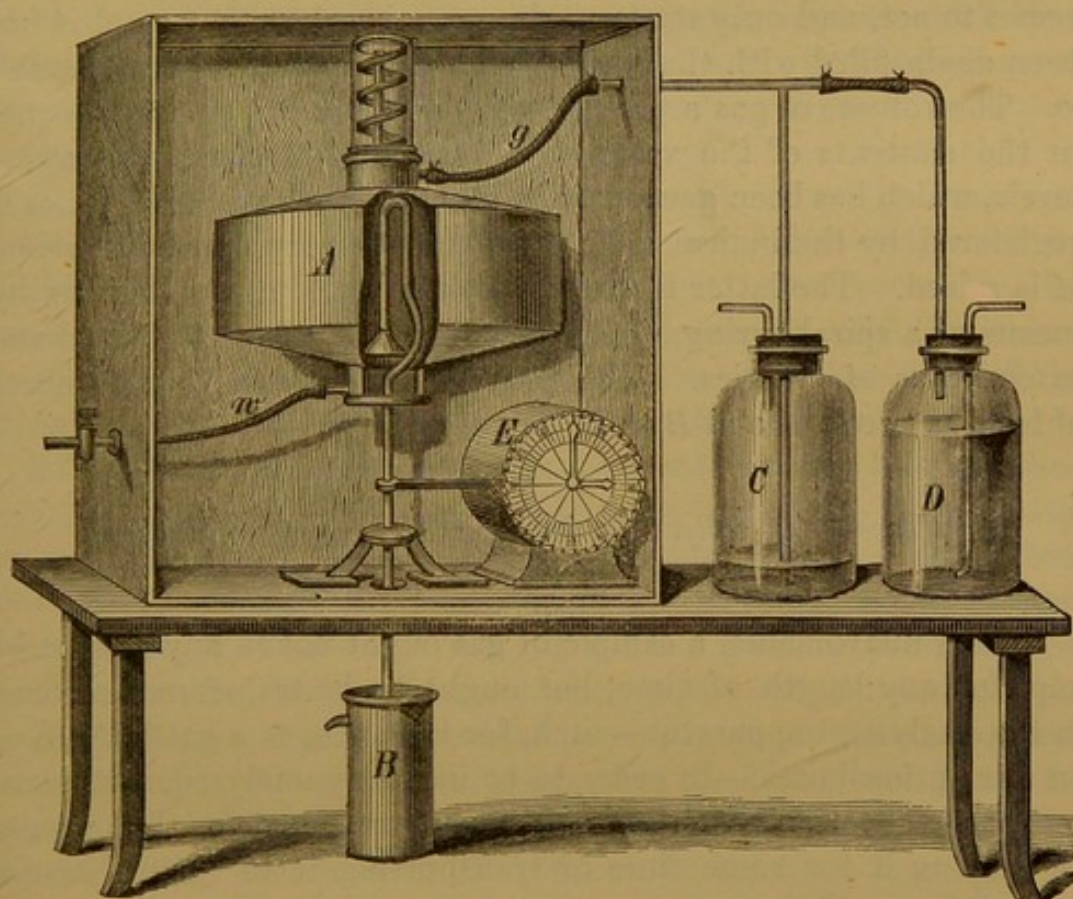
is a metal vessel A, containing on the inside a siphon whose shorter, funnel-shaped limb reaches down to the lower part of the vessel, whilst the longer limb is carried through its bottom and dips into the vessel B in which is water at a constant level. Through the india-rubber tube w, connected with the water-service, the vessel A can be filled with water. The tube g serves

C

for the entrance and exit of the gas; it communicates with the bottles C and D, the first of which serves as a water-lute, the second for containing the absorbing liquid through which the aspirated gas is to be passed. The apparatus begins to work as soon as the tap of the service-pipe is opened and water enters into A. Whilst this vessel is filling the gas contained in it escapes through the bottle C; but as soon as the water-level is up to the bend of the siphon, this begins to act and the water flows into the vessel B. If the supply of water through w is regulated so that it is less than the outflow into B, the level of water in A must sink, and the gas will be aspirated through the absorbing bottle D, from which it passes into A. But as soon as the water has run off to the end of the shorter limb of the siphon, the latter ceases to act, and only starts working again when the vessel A has been again filled with the water which continuously flows through w. The volume of gas aspirated every time the siphon acts is equal to the contents of the vessel A between the highest and lowest levels, which has been gauged once for all; the number of times is registered by the indicator E, which moves every time the vessel A is raised. The latter is hung from the top of a portable box by means of a spiral spring, which is compressed when A is filled and extended as A empties. This contrivance causes the differences of level between A and B to be equalized.

3. Vessels for collecting, keeping, and carrying Samples of Gases.

Unless unavoidable, a sample of gas ought not in any case to be kept for any length of time, but ought to be transferred at once to the analytical apparatus—such, for instance, as a gas-burette or an absorption-bottle—in order to be instantly analyzed. If, however, the collection of the gas in a separate vessel for the purpose of keeping it for some time or transporting it to some distance cannot be avoided, care must be taken not merely to exclude the air completely from it, but also completely to remove the water employed in taking the sample, as this would otherwise exercise a solvent action upon some of the constituents of the gas. This holds good for all cases in which the collecting-vessel itself is used as an aspirator, by filling it with water and causing the gas to be aspirated by the outflow of the water. If the sampling takes place

without contact with water, by pumping the gas by means of an india-rubber pump into the dry collecting-vessel or by aspirating it through the same by means of an aspirator, this must be continued long enough to ensure the complete expulsion of all air.

India-rubber collecting-vessels are, as a rule, to be avoided, because many gases are diffused through their walls, even if thick or impregnated with grease. This is the case to a very considerable extent with sulphur dioxide and hydrogen; whilst, for instance, mixtures of oxygen, nitrogen, carbon dioxide, and carbon monoxide (that is, the gases produced by combustion of fuel) can be kept unchanged in such vessels for several hours, but never till the next day.

Glass collecting-vessels, which are usually employed in the shape of tubes, are only absolutely and permanently tight provided they terminate in capillary ends which are sealed by the lamp after introducing the gas. If the enclosed gas is afterwards to be transferred to a gas-burette, narrow india-rubber tubes are attached to both ends; these are filled with water and closed by means of glass rods or pinch-cocks, after which the sealed ends may be broken within the india-rubber tubes by external pressure. In most cases, however, it is sufficient to close such collecting-tubes from the outset with india-rubber stoppers, or tubes stopped by means of glass rods or pinch-cocks (figs. 15 and 16).

In this case the end of the tube, provided with the india-rubber tube, is connected with the gas-burette, previously filled with water; the other end is made to dip into a vessel also filled with water; the cork &c. is opened below the water, and the water contained in the burette is run off till the gas has been carried into the burette, water taking its place in the collecting-tube.

Zinc collecting-vessels are especially employed for containing and transporting larger volumes of gases; and they have been found to answer very well in all cases in which the metal does not act upon the gas. The best form is that shown in fig. 17. The vessel is 50 centimetres long, or 60 centimetres including the conical ends, and has a diameter of 16 centimetres, so that it holds 10 litres of gas. Both ends have necks of 15 millimetres width, which can be tightly closed by soft india-rubber corks or by the well-known porcelain knobs with india-rubber padding, which are pressed down by a hinge and lever. The vessel is hung from three thin brass chains, fitted at the top in a ring, and can thus be con-

veniently carried by hand, even when filled with water, in order to take a sample of gas in the proper place. If the outflow is to be slow or capable of being regulated, the solid corks are replaced

Fig. 17.

Fig. 16.

Fig. 15.
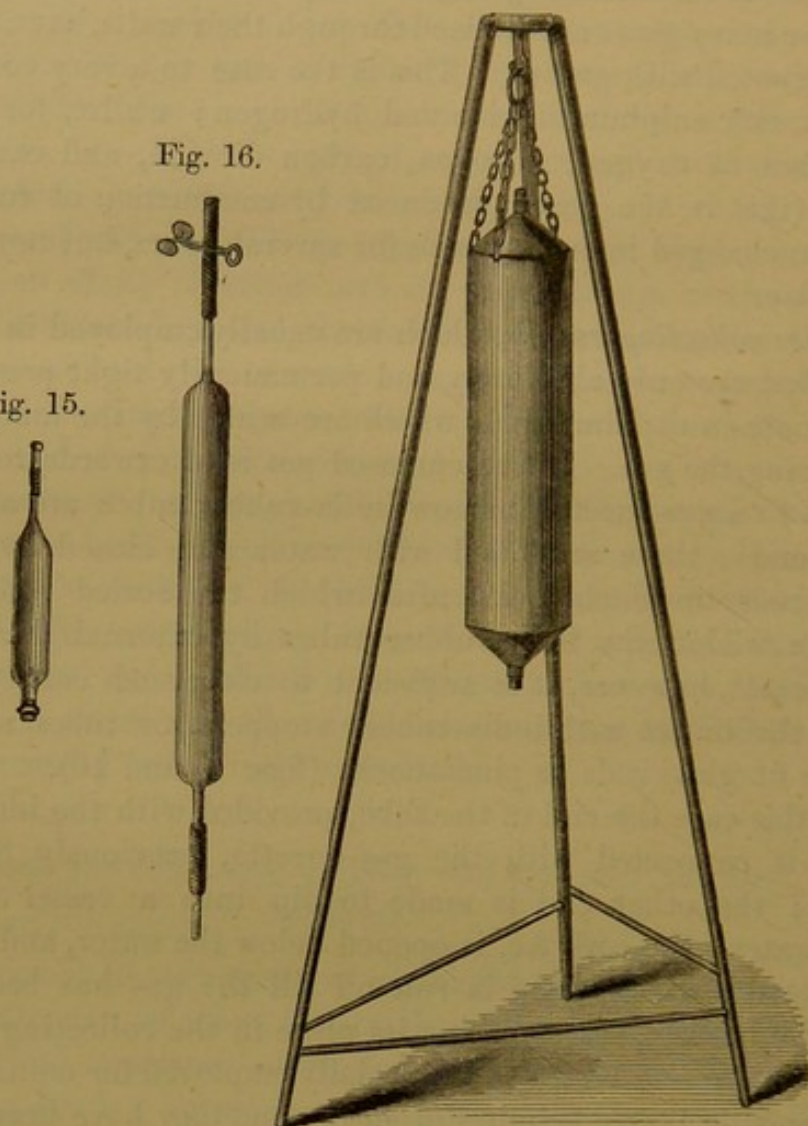
by others fitted with glass tubes and provided with screw pinch-cocks. Such vessels are employed in large numbers for taking samples of pit-gases in the Saxon coal-pits, and sending them for analysis to the laboratory of the Freiberg Mining Academy.

CHAPTER II.

ON THE MEASUREMENT OF GASES.

General Remarks. Corrections.

THE volume of a gas can be found directly or indirectly. It is estimated, either

1st, volumetrically;
2nd, by titration; or
3rd, gravimetrically.

The quantity found is in all cases expressed in *per cent. by volume.*

Every gas has the tendency to expand and fill any space offered to it; it possesses a definite *expanding power*, which, in the state of rest, is exerted as a permanent pressure, the amount of which is called the *tension* or elastic force of the gas. All gases under the same (ordinary) circumstances possess the same tension; they all are subjected to the same law as to their expansion and contraction.

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

1st, the pressure;
2nd, the temperature;
3rd, the state of moisture.

We measure gases in their condition at the time at which the measurement is made; that is, at the atmospheric pressure as indicated by the barometer and at the temperature as indicated by the thermometer; and finally, since we work with water as the confining liquid, always in a state of complete saturation with moisture. Hence the conditions under which gases are measured may be very different, and may vary during the analysis even from one

observation to another. Every such change, unless duly taken into account, might cause very considerable errors. Hence it is indispensable, in many cases, to make *a correction*, consisting in reducing the volume of gas, which is observed in varying but known conditions, to that volume which it would possess at the normal barometric pressure of 760 millimetres, at the normal temperature of 0° C., and in the dry state. By general consent this is considered as the *normal state of a gas*.

The reduction of the volume of a gas to the normal state is made by aid of a formula derived from the following observations :—

1. *Pressure.*—According to Boyle's law the volume of a gas is in inverse ratio to the pressure upon it. Hence, if

V_0= the volume at normal pressure sought,
V = the volume at the barometric pressure B,
B = the state of the barometer at the time of the observation,

we shall have

$$V_0 = \frac{VB}{760}.$$

2. *Temperature.*—The expansion by heat of a gas is $\frac{1}{273}$ of its volume at 0° for each degree Centigrade.

Hence, if a gas measures 273 cub. centim. at 0°, it will measure $273+1$ cub. centim. at 1°, and at $t°$ $273+t$ cub. centim. If, therefore,

V_0= the volume of the gas at the normal temperature,
V = the volume of the gas at the temperature t,
t = the degree of temperature at the time of observation,

we shall have

$$V_0 = V\frac{273}{273+t} \quad \text{or} \quad \frac{V \times 273}{273+t}.$$

3. *State of Moisture.*—When a gas is saturated with moisture by contact with water, it takes up always the same quantity of water in the same conditions. This water is itself transformed into the gaseous state; it therefore exerts a certain pressure, and this pressure, *the tension of aqueous vapour*, increases with the temperature, owing to the increased formation and expansion of that vapour. That tension, expressed in millimetres of mercurial pressure f, has been determined experimentally (compare Appendix), and must be deducted from the observed barometric pressure $(B-f)$.

From the preceding considerations we deduce the following *formula, which embraces all corrections* :—

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

Suppose a gas, saturated with moisture, to occupy a volume of 1000 cub. centims. at 738 mms. barometric pressure and 20° C.; its volume in the dry state, at normal pressure and temperature, will be

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

The reduction of the volumes of gases to the normal state may be omitted in analytical estimations which are rapidly performed, as material changes of pressure and temperature are not then to be expected; so also in cases in which only approximately correct results are required.

When a gas is estimated by titration or by gravimetric analysis, its volume is found at once 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 former for the volume which it would occupy at the then existing barometric pressure and temperature, and in a state of saturation with moisture.

The following formula serves for *reducing the volume of a gas from the normal state to that which it would occupy at a different barometric pressure and temperature, and in a state of complete saturation with moisture* :—

If V = the volume of the gas at the barometric pressure B and the temperature t, saturated with moisture,

V_0 = the volume at 760 millims. pressure, at 0° C., and in the dry state,

we have

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

The *observation of the atmospheric pressure* is best made by means of *Bunsen's siphon barometer* (fig. 18), which is provided with a millimetre scale etched on each of its limbs, and is held in a vertical position by the aid of a stand. The reading is made with the telescope of a cathetometer (p. 28), which is

placed at a distance of 2 or 3 metres. The sum of the readings on both limbs indicates the barometric pressure. In certain cases it is sufficient to employ a small aneroid barometer.

Fig. 18.

Fig. 19.
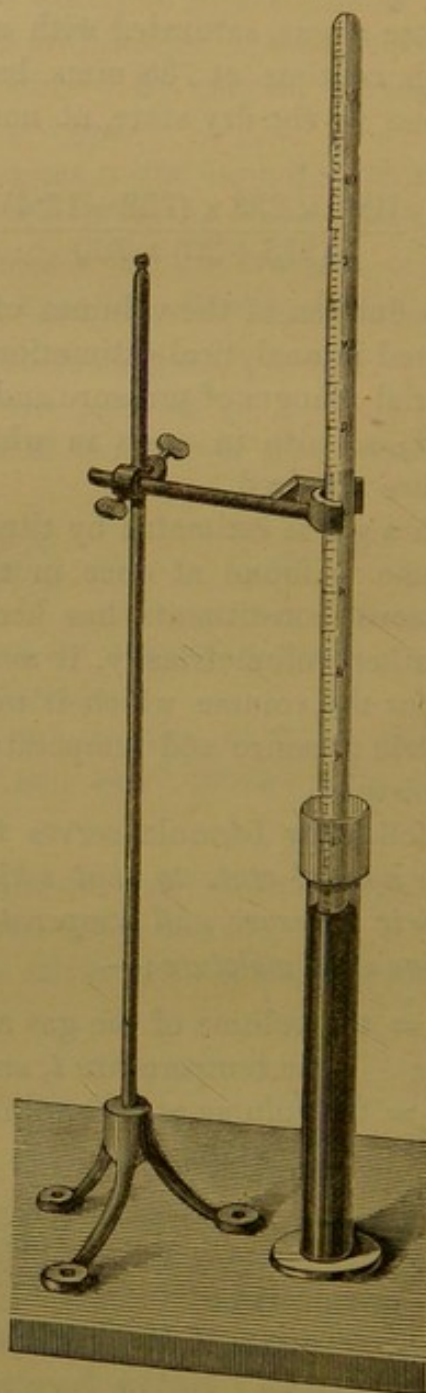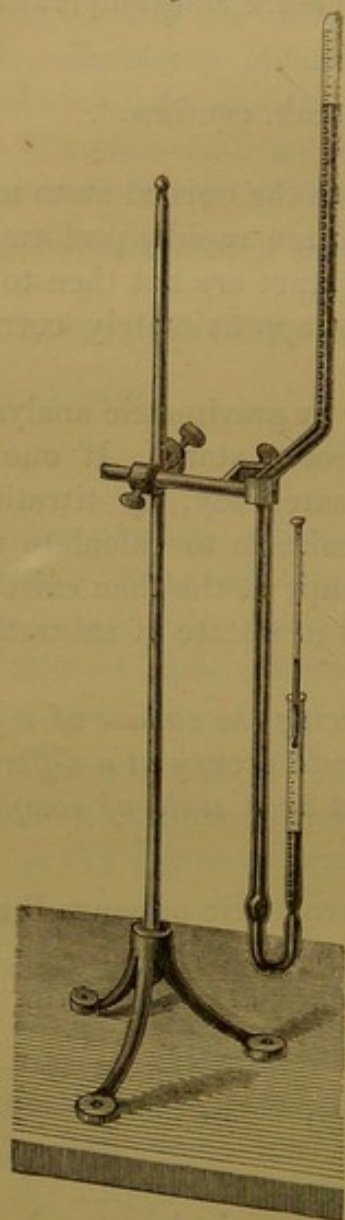
The *temperature* is observed by means of a small thermometer, divided into tenths of a degree, which is loosely placed in the shorter limb of the barometer.

We describe here also an *apparatus for rapidly reducing the volume of gases to the normal state without observing the thermometer and barometer*, which dispenses with the necessity of spending much time over calculations—an advantage to be appreciated in technical gas-analysis, where the first consideration frequently is to arrive rapidly at the result. This apparatus (fig. 19) consists of a glass tube, about a metre long and holding about 120 cub. centims., provided with accurate graduation up to 120 cub. centims., each centim. being divided into tenths, and the zero-point being at the closed top of the tube. The latter is moistened inside with a little water, and enough mercury is poured in so that the latter, on inverting the tube, previously closed with the finger, reaches above the 100 c. c. mark. The tube, held in this position, is lowered into a glass cylinder filled with mercury. The existing state of the barometer and thermometer is accurately observed; and the volume is calculated which 100 c.c. of air, taken in the normal state, would occupy under the given circumstances, by the formula

$$V = \frac{(760-4\cdot5)\,100 \times (273+t)}{273\,(B-f)}.$$

Air is now admitted by means of a glass tube drawn out into a fine point, from a gas-holder shut off by a screw-clamp, or a gas-burette, till the mercury, on the inside and outside levels arriving at the same height, has sunk exactly to the mark corresponding to the calculated volume. In this way a volume of air has been confined which is saturated with moisture, and which in the dry state and at normal temperature and pressure would be exactly $=100$ c. c. This volume increases or decreases with each external change of temperature or pressure in the same ratio as the volume of gas to be analyzed, if kept in the same locality. In order to find the latter volume, the inner and outer levels being equalized, a reading of the above apparatus is made, and the number read off is introduced into the following ratio :—

$$V : V_0 :: V^1 : V_0^1,$$

where

$V =$ the volume of air in the tube as observed under the existing temperature and pressure,

$V_0 =$ the same in the normal state (*i. e.* always $= 100$),

$V^1 =$ the volume of the gas under examination as observed,

$V_0^1 =$ the same in the normal state.

An apparatus which performs the inverse function, viz. *for rapidly reducing the volume of a gas taken in the normal state to that which would prevail under changed temperature and pressure, and in the moist state*, is constructed by filling the above-mentioned tube—after observing the thermometer and barometer and moistening the tube within—with a volume of air calculated from the formula

$$V = \frac{100(273+t)760}{273(B-f)}.$$

After equalizing the two mercurial levels and reading off, the volume V^1 is found from the proportion

$$V_0 : V :: V_0^1 : V^1.$$

Here also V_0 is constantly $= 100$ c. c.

I. DIRECT VOLUMETRICAL ESTIMATION.

A. *Measuring in Gas-burettes.*

For measuring small volumes of gases, from 0.1 to 100 c. c., we employ *gas-burettes* of various construction. These are cylindrical glass tubes, usually graduated in cubic centimetres, which can be closed at the top and bottom by glass cocks or pinch-cocks, or a water-joint, and whose division begins or ends at the upper tap. When the graduation is not required to extend the entire length of the tube, the upper portion is usually blown into a bulb or a wider cylinder, so that the tube is shortened, which may be useful for practical purposes.

In order to protect its contents from the disturbing influence of the outer temperature, the measuring-tube is frequently surrounded by a *water-jacket*, formed by a wide glass tube, closed at top and bottom. This may be provided with a strip of opaque glass, placed behind the graduation, so that the marks (which are blackened in this case) appear on a white back-ground.

The gas-burette may be put in communication with a second glass vessel, the *level-tube* or *level-bottle*, containing the confining liquid (*i. e.* water), and sometimes the absorbing liquid. This liquid serves either for confining the gas or transporting it into special absorption-vessels, as well as for regulating the pressure, which must be the same at each reading. The readings are usually made

at the pressure of the atmosphere, sometimes adding the pressure of a given, and always equal, column of water.

Pure water is the best *confining liquid*. The advantages frequently sought to be obtained by employing saline solutions, glycerine, or oils, are entirely illusory; for gases, which are relatively easily absorbed by water, are also taken up by those other liquids to such an extent that the diminution of errors obtained in this way is out of proportion to the inconveniences incurred. The above object is attained much more conveniently and simply by taking a definite quantity of the gas confined in the dry state, and estimating therefrom the constituents which are easily soluble in water, whilst only the portion which is not absorbed is received into a burette filled with water.

There are additional reasons for filling the gas-burette—that is, the measuring-vessel proper—with nothing but water if possible. To introduce the absorbing liquids into the burette, as is done in the older descriptions of apparatus, involves errors, as those liquids (*e. g.* solution of caustic potash or sulphuric acid) have a degree of viscosity quite different from that of water; they adhere much more to the glass and require much longer time for running down and collecting at the bottom.

Even in the case of pure water, *the running down of the confining liquid* must be waited for before taking a reading. Without this, errors amounting to ½ per cent. and upwards may be made. Although the state of the surface of the glass considerably influences the degree of adhesion, still the running together of the liquid in well-cleaned burettes takes place with sufficient regularity. The time required for this depends, of course, on the length of path which the liquid has to flow down in the burette. If, say, there is only 10 c. c. of gas in the burette, the level of the liquid will be constant in half a minute; but if there is 100 c. c. present it will take five or six minutes before all the water has run down. In very accurate analyses, or when estimating a very slight amount of gas from a mixture by absorptiometrical methods, this circumstance must be taken into account; but generally it is sufficient to wait a couple of minutes before each reading, and to keep the gas in the meanwhile at a slight underpressure, before the levels are equalized and the reading is taken. The error will then rarely exceed 0·1 c. c.

The *reading* itself is taken at the lower concavity of the meniscus

of the liquid (fig. 20), where the coincidence with one of the marks of the graduation is clearly recognized. Exact readings are taken by means of a magnifying-glass, or preferably, with great precision and certainty, through the telescope of a *cathetometer* (fig. 21), such as serves for barometrical and thermo-

Fig. 21.
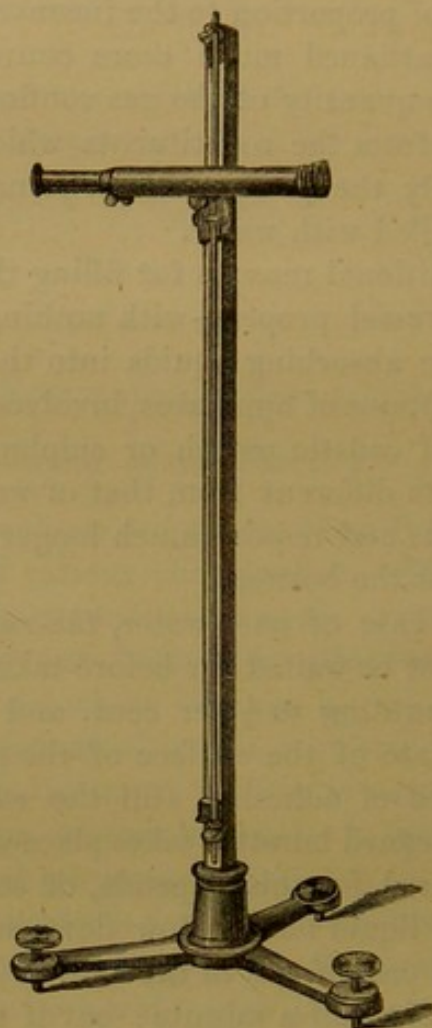

Fig. 20.

metrical observations. This telescope slides up and down a triangular brass column, and can be easily adjusted in any place by a rack and pinion. The observations with it are best made from a distance of 2 or 3 metres.

B. *Measuring in Gas-meters.*

Gas-meters serve for measuring larger or indefinitely large volumes of gas, and are only rarely used for our purposes. They

are mostly used in those cases in which a compound present in minute quantity in some gas 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 either by titration or gravimetrically.

A gas-meter 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 the former are employed in gas-analyses.

The wet or hydraulic gas-meter (figs. 22 and 23) consists of a

Fig. 22.
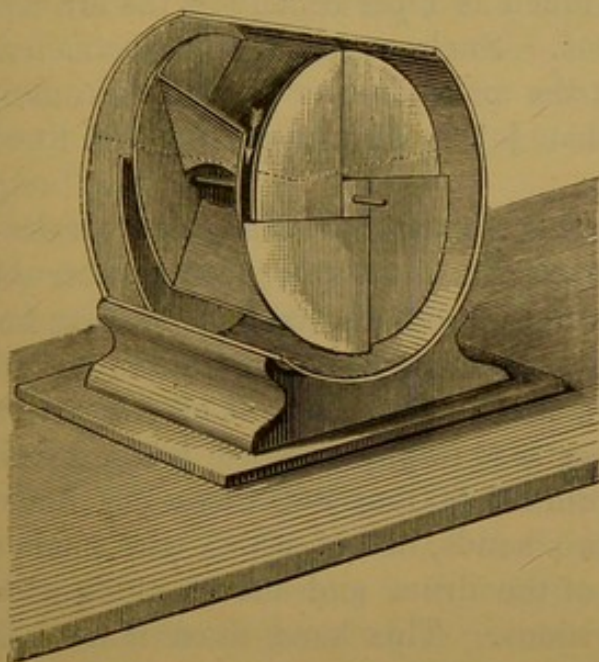
Fig. 23.
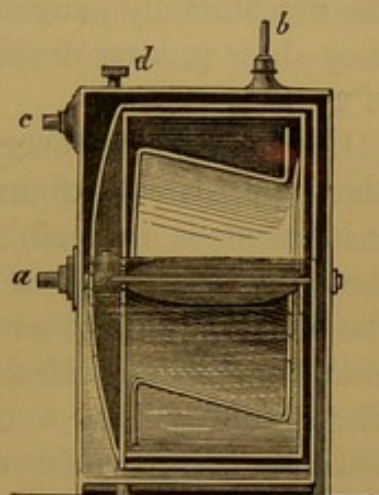
cylindrical sheet-iron vessel, resting horizontally on a base, filled to a little above half its height with liquid (water or glycerin of spec. gravity 1·14), in which moves, about a horizontal spindle, a drum divided by diaphragms into several chambers of exactly equal capacity. There are usually four such chambers, each of them provided with an opening near the spindle for the entrance of the gas, and an outlet-opening situated 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, produced 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.

In the case of the gas-meter shown in the diagrams the luting liquid is filled in by the plug *d*; the gas enters at *a* and escapes 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-analyses the smallest descriptions of meters, known as *experimental gas-meters*, are used, as is the practice at the gas-works themselves for photometrical purposes. These are 36 centimetres high and 33 centimetres long; they pass a maximum of 500, a minimum of 10, litres of gas per hour. Their indications *may* deviate from the truth by as much as 1 per cent., but the error is usually not above 0·1 per cent. Such experimental gas-meters are not officially gauged; but the makers never send them out if they show greater deviation than $\frac{1}{4}$ per cent. on passing 200 litres of gas.

Gas-meters are never altogether reliable; but they give serviceable approximate figures, especially if merely the number of revolutions is noticed, as shown by the dials, without looking for the absolute volume of the gas passed. Such restricted, but all the more correct observations, are made by means of *gas-meters with arbitrarily divided dials*, as used in physiological laboratories. These meters pass a maximum of 500 or 600 litres per hour. Their dial is provided with two hands, one of which (the smaller one) is fixed to the spindle of the drum and moves along with it, indicating the smaller divisions. This hand must make 100 revolutions before the second (larger) hand has completed one. The contents of the drum is 2·5 litres; and this volume corresponds to one revolution of the smaller, or $\frac{1}{100}$ of a revolution of the larger hand. The dial has two circular divisions. The outer circle is divided into 100 parts, numbered from 5 to 5; an entire revolution of the large hand indicates 250 litres, $\frac{1}{100}$ of it 2·5 litres. The inner circle is divided in $\frac{1}{10}$, $\frac{1}{50}$, and $\frac{1}{250}$, the divisions being marked by various lengths. The fifth part of the smallest division, corresponding to $\frac{1}{1250}$ of the inner circle, or 2 cub. centim., can be read off with certainty.

Every gas-meter ought to be checked 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, the water which runs off being collected in litre-flasks. The volume of the water run off is equal to that of the air employed, if the pressure-gauge indicates an equilibrium both at the beginning and the end of the experiments.

In certain cases *gas-meters which shut off automatically* are employed; these work till a certain volume, *e. g.* 100 litres, of gas, has passed through, whereupon a lever arrangement shuts off the entrance-tap without the help of an attendant.

II. Estimation by Titration.

Sometimes a gas can be quantitatively estimated by a reaction which takes place on its contact with unstable absorbents, and is manifested by the formation of a precipitate, a change of colour, and the like. Wherever possible this estimation is made by titration, and this is best done by means of solutions standardized, not with reference to the weight, but to the *volume* of the gas in question.

A *normal solution* is that of which one c.c. corresponds to exactly one c. c. of the gas to be absorbed, assumed to be in the normal state, *i. e.* at a pressure of 760 millims. of mercury, at 0° C., and in the dry state. A *decinormal* solution is one of which 1 c. c. corresponds to 0·1 c. c. of the gas. Where a gas is not estimated directly, but by re-titration, two standard liquids are required, which, if normal, are of course equivalent; if from practical reasons one or the other of these cannot well be brought to the precisely normal state, it is sufficient to obtain an exact measure of their mutual quantitative value.

The two following methods may be employed for estimating a gas by titration :—

A. *Titrating the absorbable constituent while measuring also the total volume of the gas.*

In this case the gas to be analyzed is generally measured in a flask of known capacity, bearing a mark in its neck, up to which the caoutchouc cork which serves for closing it is pressed down. This cork has two perforations, usually closed with bits of glass rod; but they have also to receive the delivery-tubes necessary for filling the flask, and the ends of the pipette or burette used in

titration (fig. 24). By gently loosening the glass rods in question it is easily possible to do away with any excess of pressure in the flask, or to allow the gas, displaced by liquids running into the flask, to escape without any actual opening of the vessel. If any of the constituents of the gas confined in the flask are to be removed by absorption, for the purpose of being estimated, an exactly measured volume of the normal solution of the absorbent, in excess of the necessary quantity, is introduced by means of the pipette; whilst, at the same time, an equal volume of gas is allowed to escape by loosening the glass-rod stopping in the aforesaid manner. The latter volume is, of course, deducted from the originally employed volume of the gas. After the gas has been thoroughly brought into contact with the absorbent by agitating the flask, the excess of the absorbent is estimated by re-titrating; the difference between the two volumes of liquid, if normal solutions have been employed, at once indicates the volume of the absorbed gas in the normal state.

Fig. 24.

On the same principle are founded those methods by which the gas under examination is measured in a gas-meter, and is afterwards passed through an absorbing vessel charged with a measured excess of standard absorbing liquid.

B. *Estimation of the absorbable constituent when the non-absorbable residue of gas is measured.*

In this case the gas under examination first passes through an apparatus containing a known volume of titrated absorbing liquid (normal solution), and after that through the measuring apparatus which indicates the volume of the non-absorbable portion of the gas. The sum of both amounts, that found by titration and that measured directly, corresponds to the total volume of gas employed.
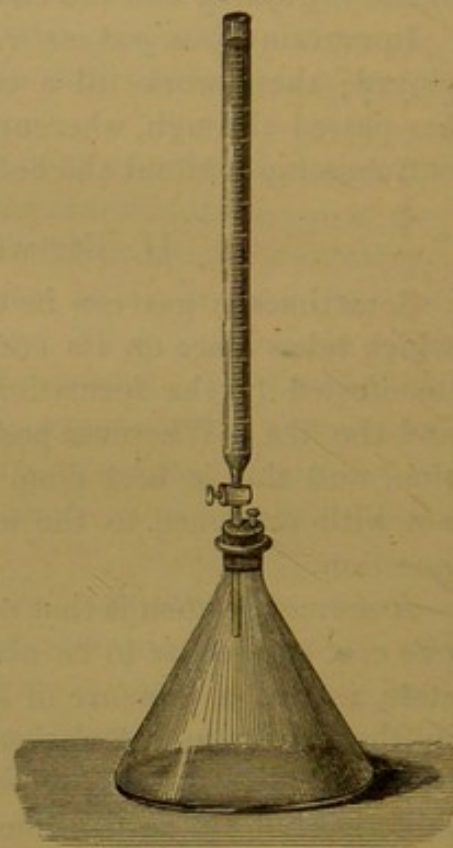
The process pursued may be either that described under A, namely, employing a measured excess of the absorbent and re-titrating; or else the quantity of the absorbent is limited, but the gas is passed through till a visible reaction, for instance a change of colour, proves that the absorbent has been completely used up. In the former case the titration is an indirect, in the latter a direct one.

The volume of that part of the gas which is not absorbed is found by a measuring apparatus attached to the absorption-vessel, and either connected with an aspirating arrangement, or itself acting as such. According to the bulk of the volume of gas to be measured, and to the accuracy to be attained, we employ as a measuring apparatus either a *gas-meter*, or a *water-aspirator*, or an *india-rubber pump*, which pumps at each stroke approximately equal volumes of gas. If the estimation of the absorbable portion is effected by retitration, that is if a known excess of the absorbent is employed, the experiment may be continued till the non-absorbable portion has reached a definite volume; this can be measured either by a gas-meter which shuts off automatically, or by an aspirator filled with a known quantity of water, to be run off completely. In that case the non-absorbable portion of the gas is a constant, the absorbable portion a variable magnitude.

If the titration is to be a direct one, the volume of the absorbable gas is given by the volume of the normal solution employed, whilst that of the unabsorbed portion is variable, and is found by a gas-meter, by the number of strokes of a pump, or by collecting in a graduated cylinder the water that runs out of an aspirator.

In the processes mentioned under A and B, the absorbed gas is measured in the normal state, but that which is not absorbed is taken at the then existing pressure and temperature of the atmosphere, and in the moist state. If the result is to be correct both volumes must be reduced to like conditions, but it is immaterial whether the uncorrected or the corrected volumes are chosen for this purpose.

III. Gravimetrical Estimation.

Finding the volume of a gas by estimating its weight presupposes its previous absorption and transformation into a solid or liquid compound, capable of being weighed. This kind of estimation is

D

but rarely employed; principally for treating gaseous constituents present in minute quantities. These are absorbed, and the volume of the gases measured exactly as described under No. 2, A and B, for estimating gases by titration; where it is not sufficient to determine the increase of weight of the absorbent, the compound absorbed must be transformed into an insoluble precipitate in order to be ultimately weighed.

IV. ARRANGEMENT AND FITTINGS OF THE LABORATORY.

A person who has to carry out gas-analysis for technical purposes is required, in very many cases, to work in anything but a properly fitted-up laboratory. He may be compelled to put up his apparatus and take samples of gases in the most various places—at furnaces, flues, and chimneys, in open yards, in the field, or even below ground, and, if possible, to perform the analyses in these same places. It is evident that in working at such temporary stations the accuracy of the results may be seriously impaired by unfavourable circumstances, since it is sometimes quite impossible to avoid disturbing influences.

It is different in the laboratory. Here all arrangements can and must be provided which make it possible to work quickly and conveniently, as well as accurately, and this should apply even to temporary conditions of working, at least to a certain extent.

The *laboratory* should be a room exposed in the least possible degree to variations of temperature. Its walls ought to be thick and not too much exposed to the sun; the windows ought to give a good light and to be as nearly as practicable turned towards the north. If the room must be heated, this is best done by a stove (like the American stoves), which is lighted the night before, and then kept continually burning, so that the room and the objects contained in it are equally warmed throughout, and the action of radiant heat during the day is as much as possible avoided.

The temperature of the apparatus, the reagents, the water, and the absorbing-liquids should be the same as that of the laboratory; they should therefore be kept in the laboratory, and not in a different room. In order to ensure a supply of water of equable temperature for confining the gases, brackets are fixed against the wall at suitable distances, about 5 feet above the working-bench, on which are glass bottles or japanned tin vessels kept constantly full of distilled or pure well-water. They are provided at the bottom with a

neck, fitted with an india-rubber stopper with a somewhat wide glass tube bent downwards at a right angle, to which is attached an india-rubber tube hanging down upon the working bench, with a glass end and a strong pinch-cock. When out of use the glass end is placed in a small glass cup, attached to the wall so as to avoid any swaying of the tube and any dropping of water (fig. 32).

The *working benches* are provided with drawers for keeping the requisite stores of india-rubber, glass, capillary and combustion tubing of different bores, of T-pieces and junctions, pinch-cocks, test-papers, and so forth. Some small tables are surrounded with a bevelled wooden ledge; they are made to shelve forwards to the centre, and a circular hole is made in the deepest place, in which a glass funnel and down-pipe are fixed. The top of the table is afterwards covered with thin sheet lead; above the funnel a hole is cut in the lead, and the latter is evenly laid against the inner side of the funnel; it is also turned over the wooden ledge. Such tables serve for working with corrosive liquids, which, in this case, may be run off straight away, and entirely removed by rinsing the table with water.

The laboratory must be provided with a *water supply* for filling the stock-vessels, gas-holders, and aspirators, and for feeding the

Fig. 25.
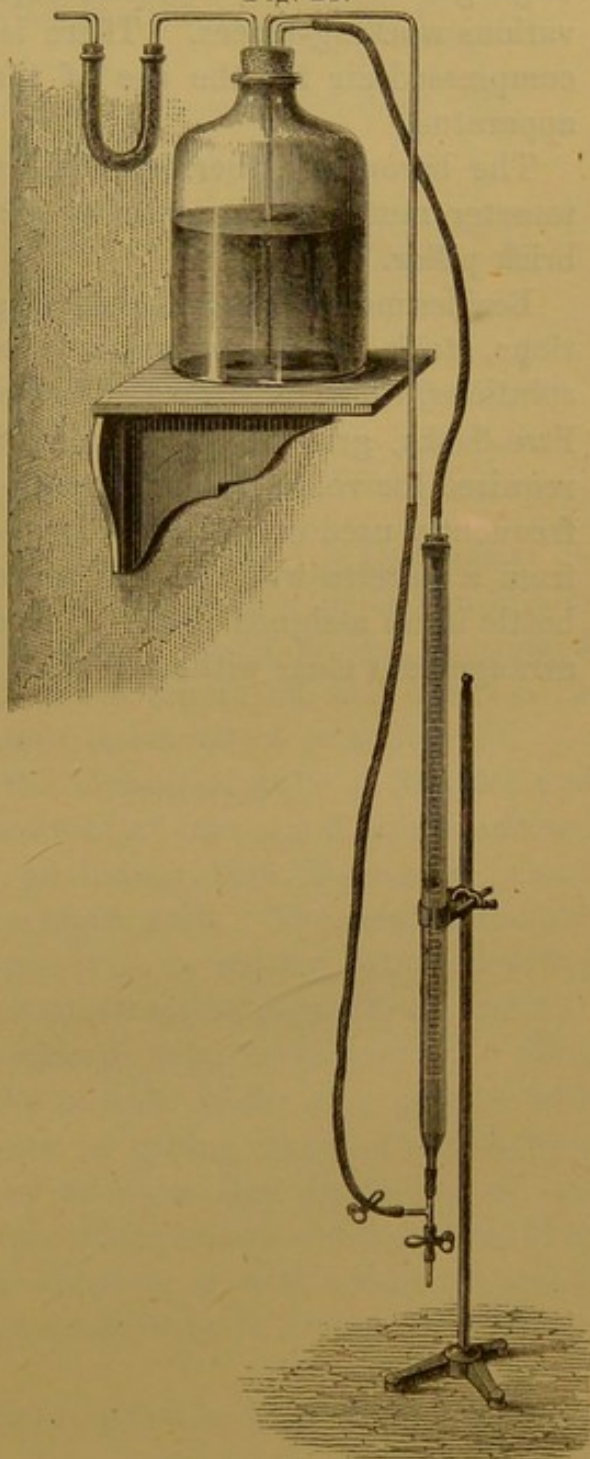
water-jet pumps, as well as with a *sink* for cleaning the apparatus. There should also be a *gas-pipe*, with branches and taps of different bores at suitable places. The smaller taps supply the gas for heating the combustion-capillaries, the larger ones for the combustion-furnace. In the laboratory of the Freiberg Mining Academy there is also a pipe-service for the gaseous mixtures intended for the students' practice; these mixtures are kept in large gas-holders of 150-litre capacity, and are conducted to the various working-places. There is likewise a pipe for supplying compressed air for the use of the combustion- and absorption-apparatus.

The barometer, thermometer, correction-apparatus, and cathetometer must also be suitably placed; the last preferably on a brick pillar.

Besides measuring- and absorbing-apparatus of various constructions, stock-vessels for reagents, absorbing-liquids, and standard solutions, there must be a sufficient selection of burettes, pipettes, litre-flasks, graduated cylinders, and generally all the apparatus required for volumetric analyses. Standard solutions, which are frequently used or which easily undergo change, are best supplied from a burette with feeding arrangements, fixed with its stock-bottle in an assigned place. The diagram (fig. 25) will make this arrangement clear without further description.

CHAPTER III.

APPARATUS AND METHODS FOR CARRYING OUT THE ANALYSIS OF GASES.

I. Estimation of Gases by Absorption.

1. *Direct Volumetric Estimation.*

A. Estimation by means of Apparatus combining the Functions of Measurement and Absorption.

a. *Winkler's Gas-burette.*

THE apparatus described below, constructed by the author in 1872, has lost its value since that time, owing to the invention of others that are much more suitable. It is, however, mentioned in this place because it is still much employed, and because its manipulation is to a certain extent instructive for the learner.

Two communicating tubes, the measuring-tube A (fig. 26) and the level-tube B, held by the clamps of an iron stand, are connected at their lower extremities by an india-rubber T-piece d, whose free branch is usually closed by a pinch-cock. The measuring-tube A serves for receiving the gas, and is at its bottom provided with a double-bored tap, a, of peculiar construction (figs. 27, 28, and 29). One of the perforations is the ordinary transverse bore; the other one is a curve, running from the outside of the plug parallel with its length, and ending in a piece of tubing likewise closed by a pinch-cock. It is unnecessary to show that by means of this three-way tap every possible communication can be effected between either limb of the tube, with the outer air, or with a tube conveying the gas. The top of the measuring-tube is closed by a simple glass tap b.

The measuring-tube holds about 100 c. c. between the two taps.
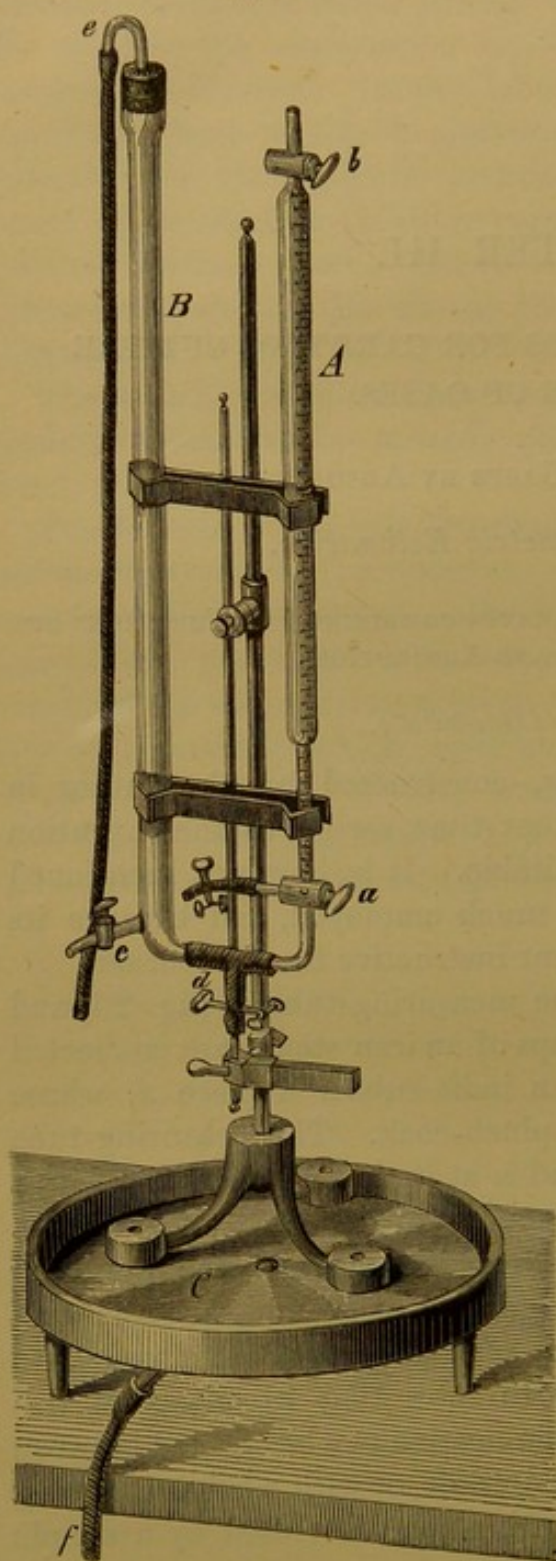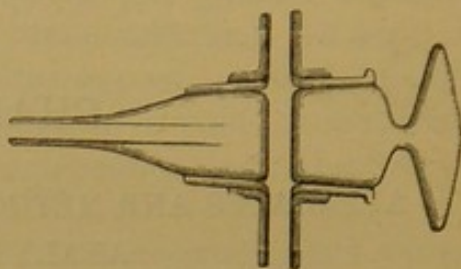
Fig. 26.
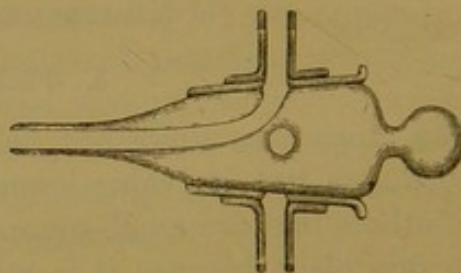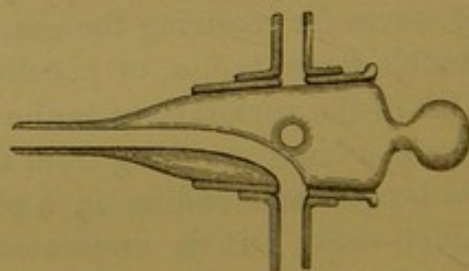

Fig. 27.

Fig. 28.

Fig. 29.

It is exactly measured once for all, and the amount etched on the tube. The tube is moreover divided from the bottom upwards into tenths of cubic centimetres, including the contracted pieces adjoining the taps, of which the lower one occupies about a quarter of the total length of the tube, and is intended for measuring small volumes; whilst the upper one should be as short as possible, to prevent any liquid from adhering to it.

The level-tube B serves for receiving the absorbing-liquid. It is closed at the top by an india-rubber cork, carrying a bent tube c, with an india-rubber tube attached to it. The lateral outlet-tap c with india-rubber tube, which increases the liability of the apparatus to fracture, is not indispensable and may be left out.

The stand is provided with a movable holder for the tubes, so that these may be placed at will either in a vertical or a horizontal position. If there is no suitable working-bench (p. 35), the apparatus is placed on a lead-covered wooden basin C, provided for the (mostly alkaline) absorbing-liquids and rinsings.

Manipulation.—Open the tap b, and by means of the tap a put the measuring-tube A in communication with the gas to be analyzed; by means of an india-rubber pump or an aspirator, cause a current of the gas to traverse the measuring-tube till all air has been driven out. According to whether this is done by pressure or by aspiration, either the tap a or the tap b is closed first in order to be sure that the sample of gas is under atmospheric pressure. The tap a is placed so that the inner end of its longitudinal bore is turned downwards (as in fig. 29).

The level-tube B is now filled with the absorbing-liquid; the air enclosed below the tap a is expelled by a momentary opening of the pinch-cock attached to that tap; and now, since the gas and the liquid are only separated by the plug, the absorption may begin. For this purpose the plug is turned 90 degrees, thus making a connection between the two tubes. The absorbing-liquid at once begins to enter the measuring-tube; by blowing into the india-rubber tube attached to the level-tube B it is forced up a little, and the tap a is turned back into its first position. By alternately placing the tubes vertically and horizontally (fig. 30) the gas and the liquid are brought into intimate contact, and this alternate movement causes the absorbable portion of the gas to be absorbed quickly. If, on again opening the tap a, no more liquid enters into the measuring-tube, the absorption is complete. The

only thing remaining is to produce the same level of liquid in the communicating tubes, which is done by opening the lateral tap *c*, or equally well by the pinch-cock *d*, leaving, of course, the tap *a*

Fig. 30.
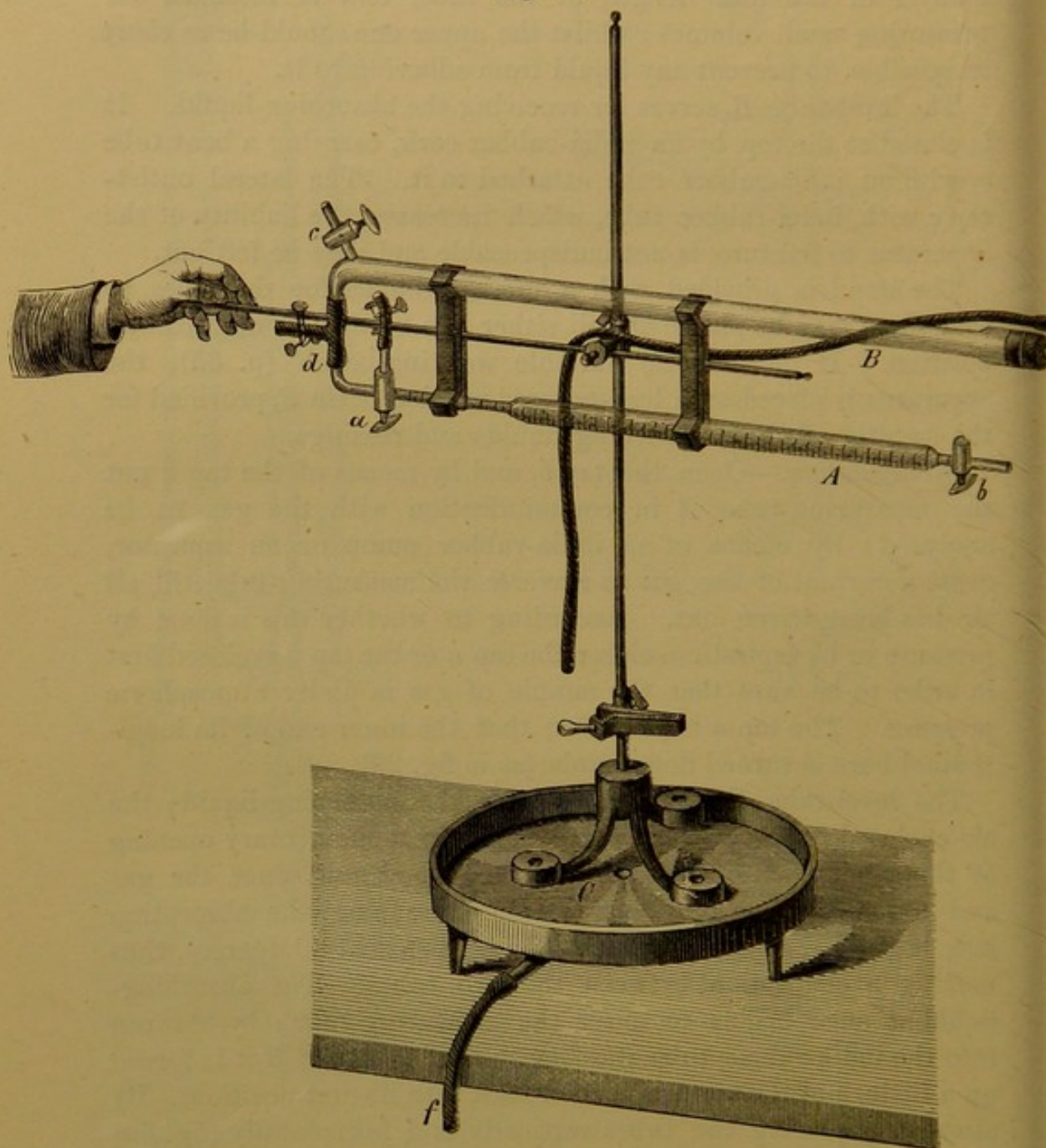
open in the meanwhile. The volume of liquid entering into *A* is equal to that of the gas absorbed, and is converted into per cent. by volume on multiplication by 100, and division by the contents of the measuring-tube.

After each estimation the apparatus is thoroughly rinsed with water; the taps are dried with blotting-paper, and are again greased, slightly but equally, all over. Whilst the apparatus is out of use the plugs of the taps should be taken out, as they frequently stick very fast when left in.

Applications :—

(a) *For estimating carbon dioxide in mixtures of that gas and air, or in the gases resulting from combustion (chimney-gases), from blast-furnaces, or lime-kilns; in the gas for saturating the lime in sugar-refining &c.* The absorbent is a moderately strong solution of caustic potash.

(b) *For estimating oxygen in the atmospheric air.* The absorption is effected by means of an alkaline solution of pyrogallol. In order to avoid an excess of this somewhat costly reagent, a sufficient quantity of a concentrated aqueous solution of pyrogallol is first poured into the level tube and brought close to the tap *a*, and then a solution of caustic potash is run in on the top of it.

b. *Honigmann's Gas-burette.*

The burette *A* (fig. 31) consists of a measuring-tube, tapering at both ends, closed at the top by a simple tap *a*; whilst the bottom end *b* is left open, and is merely provided with a piece of stout india-rubber tubing. The zero mark of the tube, which is divided into $\frac{1}{5}$ cubic centimetres, is near the bottom, and it holds up to the tap exactly 100 cub. centim. The absorbing-liquid is contained in the glass jar *C*; the elastic tube allows the burette to be plunged down to any depth.

Fig. 31.

Manipulation.—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 manufacture of sodium carbonate by the ammonia process. Gas is aspirated through it till all air has been expelled; the tap *a* is closed and the burette is immersed in the glass jar *C*, filled with a solution of caustic potash exactly to the zero mark. The tap *a* is now opened for a moment, in order to equalize the pressure within and without, and thus exactly 100 cub. centim.
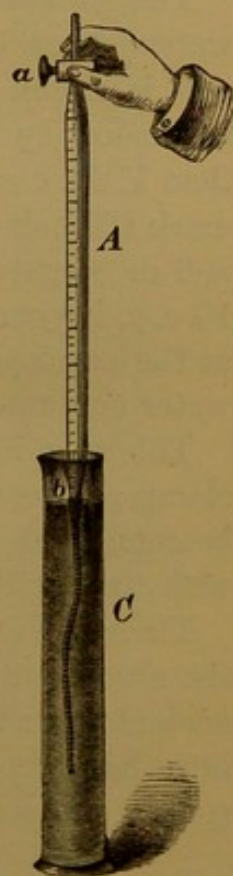
of gas are confined in the burette. The absorption of the carbon dioxide is started by immersing the burette somewhat lower, so that its inside is wetted with the potash solution, and then pulling it out so far that the end of the elastic tube remains within the liquid; but the burette itself is raised over the edge of the glass jar and can be moved about and downwards. The solution of caustic potash at once begins to enter, and after agitating a few times the absorption is complete. The burette is now again immersed in the liquid, so far that the inner and outer levels are the same, and the reading is taken, yielding directly the percentage of carbon dioxide by volume. This apparatus cannot produce absolutely accurate results; but its construction and manipulation are very simple, and the results are obtained in a few moments. After each absorption the burette and elastic tube must be most carefully rinsed with water.

Application :—

For estimating carbon dioxide in mixtures of that gas and air, in the gases from lime-kilns, for saturating the lime in sugar-refining, &c.

c. Bunte's Gas-burette.

The measuring-tube *A*, which may be entirely enclosed in a water-jacket (fig. 32), carries a funnel *t*, provided with a mark, and is closed at the top by the three-way cock *a* (comp. p. 38) and below by the plain tap *b*. The space between is rather more than 110 c. c., and is divided into fifths of a cubic centimetre. The mark 100 coincides with the plug of the upper tap *a* ; the zero point is 6 or 8 centimetres above the tap *b*, and the division is carried 10 c. c. beyond this. The gas in this burette is always measured at the atmospheric pressure, plus the pressure of the column of water contained in the funnel up to the mark.

This tube is fixed to an iron stand by means of an easily opened clamp ; a second arm of this stand carries the funnel *B*, which can be connected by an elastic tube of a width of about 3 millimetres with the capillary bottom end of the burette.

There is moreover a small glass or porcelain cup *C* for holding the absorbent, and two aspirating-bottles, whose construction is evident from the diagram. The bottle *D* serves for forcing water into the burette or withdrawing it therefrom. In both cases the rubber end *n* is put upon the tip of the burette at *b* ; whilst at the

Fig. 32.
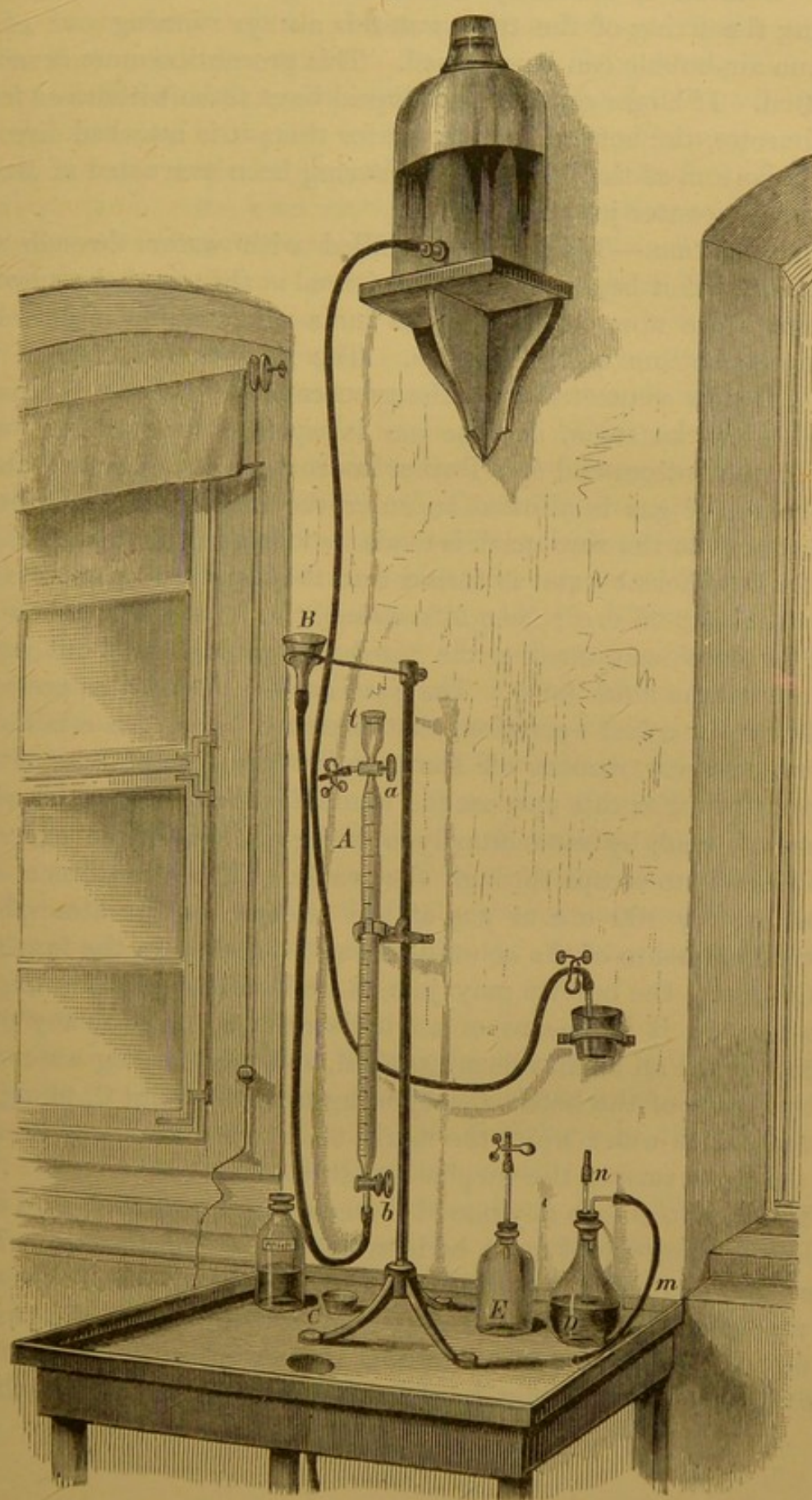
same time air is blown by the mouth into the tube *m*, so that during the fixing of the tube water is always running out of *n*, and no air-bubble can be enclosed. This precaution must *never* be omitted. If larger quantities of liquid have to be withdrawn from the burette, the bottle *E* may serve for this; it is attached directly to the bottom of the burette, after having been evacuated of air by means of a water jet-pump.

Manipulation.—The burette is filled with water through the funnel *B*, till it begins to enter the funnel at the top of the burette. The taps are now closed and the india-rubber tube is detached from the bottom of the burette. The longitudinal bore of the tap *a* is now connected with the tube conveying the gas, already filled with the same, and the gas is aspirated by running water out of the bottom end *b*. Rather more than 100 c. c., say about 105 c. c., of gas is allowed to enter the burette, 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 mark for 0. The gas is still under a plus pressure, and now, by a last operation, that pressure has to be established at which every reading-off has to take place in the case of this apparatus. For this purpose the funnel *t* is filled with water up to the mark, and, by momentarily opening the tap *a*, the excess of gas is made to escape through the water. The burette now contains 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*.

Of course the burette may just as well be filled by drawing the gas through it by means of an india-rubber pump or any other aspirator till all air has been expelled, and then forcing water into it by means of the bottle *D*, adjusting it to the point 0, filling the funnel *t* with water up to the mark, and by a momentary opening of the tap *a* raising the surplus pressure.

In order to absorb any one of the constituents of the gas, a suitable absorbing-liquid must be introduced into the burette. First the water contained in the same is drawn off by means of the bottle *D* up to the tap *b*, the latter is closed, and the end of the burette is dipped into the cup *C* containing the absorbing-liquid. If the tap *b* is now opened again, 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 the funnel end, closing the latter by the hand, and is moved up and down in short, but not violent, jerks. When the absorption is complete the tip of the burette is again dipped into the cup *C*, and the tap *b* is opened, whereupon liquid enters in the place of the absorbed gas. If, on repeating the operations just described, the liquid remains at the same level, the reading may be taken. First, however, the gas has to be put under the proper pressure by running water into the burette out of the funnel *t* (thus also rinsing its sides), and then, whilst the tap *a* is left open between the funnel and the tube, filling the funnel with water up to the mark.

Since the adhesion of the absorbing-liquids differs from that of water, it is preferable to remove those liquids by water and to repeat the reading. Both taps are opened, whilst water is run into the funnel *t* in a steady stream, and this rinsing of the burette is continued till the original reaction of the liquid has ceased. Gas cannot be lost in this way; therefore, after the water contained in the burette has been drawn off, another reagent can be introduced in order to absorb another of the gaseous constituents. In the same way a third and fourth gaseous constituent can be removed and volumetrically estimated by rinsing out and introducing suitable absorbents.

Applications :—

(a) *Estimation of carbon dioxide in a mixture of that gas and air, or in the gases resulting from combustion, from blast-furnaces, lime-kilns, gas-producers, &c.* The absorbent in this case is a moderately strong solution of caustic potash.

(b) *Estimation of oxygen in atmospheric air.* The absorbent is an alkaline solution of pyrogallol. Not to waste the latter, a concentrated aqueous solution of pyrogallol is first introduced into the burette, and this is followed by a strong solution of caustic potash.

(c) *Estimation of carbon dioxide, oxygen, and nitrogen in mix-*

tures of air and carbon dioxide, or in chimney gases. The carbon dioxide is absorbed by a solution of potash ; this is washed out and the oxygen absorbed by a strongly alkaline solution of pyrogallol. After again washing out, the nitrogen remains behind.

(d) *Estimation of carbon dioxide, oxygen, carbon monoxide, and nitrogen in blast-furnaces or producer gases.* Carbon dioxide and oxygen are absorbed as under (c), and afterwards carbon monoxide by a solution of cuprous chloride in hydrochloric acid. This is washed out first with dilute hydrochloric acid, then with pure water, and the remaining nitrogen is ultimately measured.

B. Estimation by means of Apparatus with Separate Parts for Measuring and Absorption.

The absorption of a gaseous constituent is frequently 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 carried over into the measuring-tube, and its volume is read off. The volume of the gas absorbed follows from the difference of the two readings. This process admits of thoroughly utilizing 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 essential intermediary operation, and before cleaning and refilling the apparatus.

The measuring and absorbing vessels must in this case be capable of being connected with each other in a permanent or a temporary way. This connection is usually made by a narrow capillary tube whose contents scarcely amount to $\frac{1}{10}$ c. c. ; the quantity of air contained in it, which becomes mixed with the gas under examination, is hence so slight that it does not sensibly influence the result. In special cases this capillary tube may be filled with water in order to drive out the air.

The first apparatus of this kind was constructed by C. Scheibler ; it served for estimating the carbon dioxide in the saturation-gases of sugar-works. This apparatus, like some others, for instance that of Liebig, did very good service in its time, but has now been superseded by others of simpler description.

a. *Orsat's Apparatus*[*].

The measuring-tube A (fig. 33) contains, from the zero mark
at its bottom to the upper capillary end, exactly 100 c. c., but
its graduation (in $\frac{1}{5}$ c. c.) only extends to 40 c. c. and ceases where

Fig. 33.
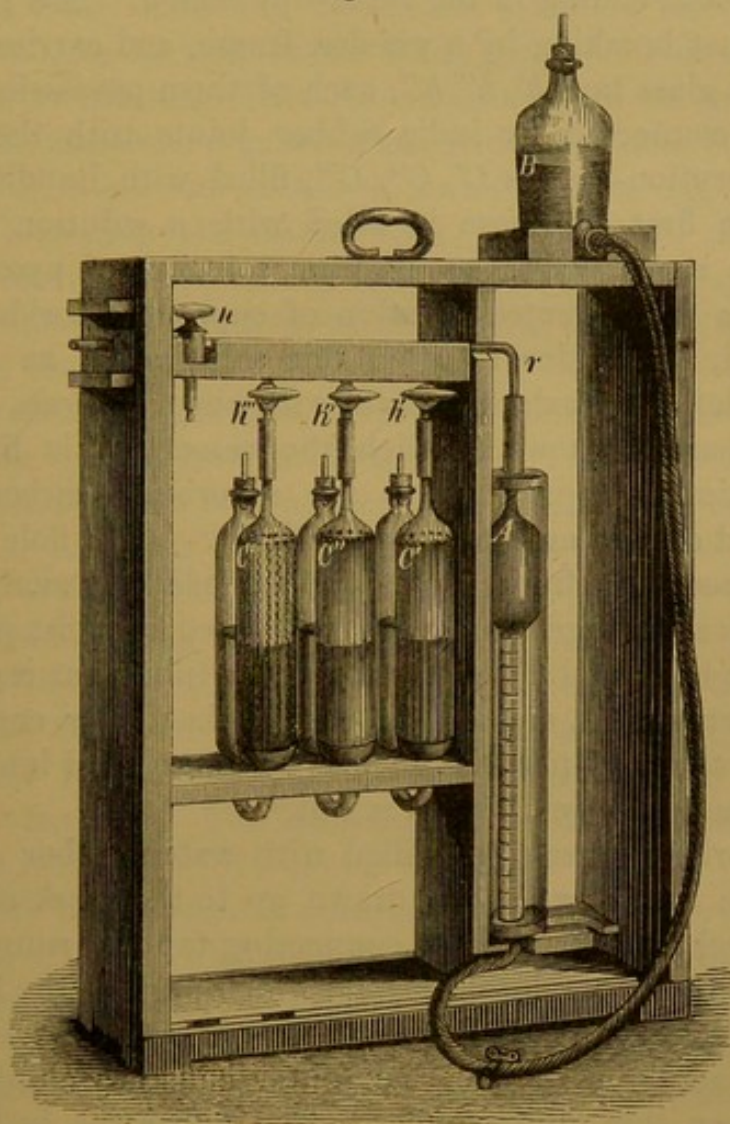
the tube is enlarged.   In order to withdraw the gas contained in
this burette from the influence of the changes of external tempe-

[*] This apparatus is an imitation of that constructed by Schlösing and Rolland,
which is much less known; both depend upon a principle first applied by Regnault
and Reiset.   It has met with an extraordinary approval, and with many modi-
fications, *e. g.* by Salleron, Aron, Ferd. Fischer, Rob. Muencke, and E. Tomson.
The author prefers the modification now constructed by Rob. Muencke of Berlin,
and therefore describes only that.

rature, the tube is surrounded by a water-jacket, closed at top and bottom by india-rubber stoppers and provided with a white background of opaque glass, upon which the black divisions of the burette are sharply visible. The bottom of the burette is connected by an elastic tube with a level-bottle B filled two thirds with water; the top end is connected with a glass capillary r, bent at a right angle and ending in the three-way cock h. This tube is protected against breaking by a wooden frame, and carries at a right angle three glass taps h', h'', h''', each of them possessing capillary tubes and connected by india-rubber joints with the three U-shaped absorption-vessels C', C'', C''', filled with bundles of glass tubes. The first of these is filled with a solution of caustic potash, the second with an alkaline solution of pyrogallol, the third with a concentrated solution of cuprous chloride in hydrochloric acid. In order to keep this solution in an unchanged state, it is left in constant contact with copper spirals, introduced into the glass tubes with which the vessel C''' is filled. The above-mentioned liquids serve for absorbing carbon dioxide, oxygen, and carbon monoxide respectively. The whole apparatus, as may be seen herefrom, is specially intended for analyzing combustion-gases. Oxygen can also be absorbed by moist phosphorus. In this case the vessel C'' contains no glass tubes, but it ends at the top in a small neck, closed by a soft india-rubber cork, through which thin sticks of phosphorus may be introduced into the water contained in the vessel till this is full*.

The absorbing-vessels are filled with water rather more than halfway up; and this is then drawn up to the mark made in the capillary neck, by opening the connecting tap and running off the water contained in the burette A, for which purpose the level-bottle B must be lowered. In order to protect the absorbing-liquids against the action of the air, their outer ends are closed by small balls of very thin india-rubber. The apparatus is fixed in a portable wooden box, closed on both sides by sliding-doors.

Manipulation.—Raise the level-bottle at the top, open the tap h,

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* Such thin sticks of phosphorus can be obtained from the dealers in chemicals; they may be made by drawing phosphorus, melted under tepid water, into glass tubes, employing an india-rubber tube for the purpose; or else they are replaced by irregular pieces of phosphorus, such as are obtained by shaking melted phosphorus with tepid water till it solidifies by the cooling of the water. (Translator.)

and allow the burette A to fill with water up to the capillary part. Connect the outer end of the capillary tube with the tube through which the gas is to be led, and the lower end of the three-way cock h with an india-rubber pump by which the air is removed from the conducting-tube. Now aspirate the gas by lowering the level-bottle B and turning the tap h through 90 degrees. Run off the water a little below the zero mark, close the tap h, compress the gas by raising the level-bottle B till the water rises above zero, squeeze the connecting india-rubber tube close to the joint by means of the fingers or a pinch-cock, and then, after lowering the level-bottle B, allow the excess of water to run out to zero by cautiously loosening the elastic tube. Last of all the tap h is opened for an instant in order to produce a pressure equal to that of the atmosphere, whereupon exactly 100 c. c. of gas will be confined within the burette.

Now the absorption begins, first of all that of the carbon dioxide by conveying the gas into the U-tube C'. This is done by raising the level-bottle B, and at the same time opening the tap h'. The absorption is hastened by causing the gas to travel several times from C to A and back, alternately lowering and raising the level-bottle and leaving the tap h' open all the time. At last the level of the liquid in C' is adjusted to the mark, and the tap h' is closed. Now the reading can be taken, after raising the level-bottle B till its contents are at the same level as the water within the burette. The decrease of volume found indicates directly the percentage by volume of carbon dioxide. In exactly the same way the oxygen is absorbed in C'' and then the carbon monoxide in C'''; the unabsorbed residue represents the nitrogen. If the oxygen is absorbed by moist phosphorus it is unnecessary to convey the gas backwards and forwards as above described; the fumes of phosphorous acid which form during the absorption and cling for a long time to the gas need not be taken into account. Oxygen is only satisfactorily absorbed by phosphorus provided the temperature of the apparatus is about $20°$ C., certainly not below $15°$ C. The estimation of carbon monoxide is not in the least influenced by the employment of phosphorus (notwithstanding Baumann's assertion); but the presence of certain gases, usually present in very slight quantities, especially that of heavy car-buretted hydrogen, considerably impairs, or even annihilates, the absorbing action of phosphorus upon oxygen.

E

Application :—

Estimation of carbon dioxide, oxygen, carbon monoxide, and nitrogen in artificial mixtures of gases, in gases from blast-furnaces, reverberatory-furnaces, or other combustion-gases.

The absorbing liquids are :—

For carbon dioxide : a solution of caustic potash of specific gravity 1·20.

For oxygen : the same solution, to which 15 or 25 grams of pyrogallol have been added for each apparatus, or, in lieu of that, phosphorus and water.

For carbon monoxide : a saturated solution of cuprous chloride in hydrochloric acid of specific gravity 1·10.

b. *Apparatus for estimating Carbon Dioxide in Gaseous Mixtures containing relatively little of it.*

The following simple apparatus, which is on the same principle as Orsat's, is convenient for estimating relatively small quantities of carbon dioxide, such as occur in pit gases and the like, which may, even if amounting only to a few per cent., considerably interfere with respiration.

The measuring-tube *A* (fig. 34) is closed at the top by a three-

Fig. 34.
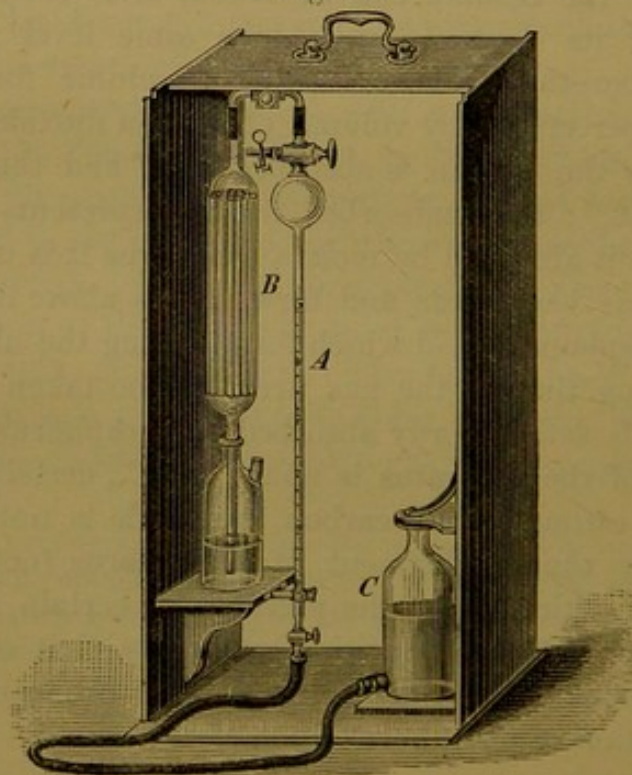
way cock, at the bottom by a simple tap. Its capacity is 100 c. c. ; the principal portion of this is contained in the globular part; the narrow cylindrical part only contains 5 c. c., and is divided into tenths of a cubic centimetre. The lower end of the burette is connected by a narrow elastic tube with the level-bottle C, containing pure water ; from the upper part a glass capillary tube leads to the absorbing-vessel B, which is filled with a solution of caustic potash up to the mark. The burette is filled with the gas to be examined through the pinch-cock attachment of the three-way cock; otherwise the apparatus is handled exactly as Orsat's. The bottom tap is necessary, because in this case the level of the water must be very finely adjusted, which is difficult to do without a tap. When the liquids contained in the communicating vessels A and C have been brought to the same level, the tap is closed and the reading is made.

Application :—

Estimation of carbon dioxide in artificially prepared mixtures of the same with air, in the gases from coal-pits, wells, caves, subsoil, tombs, from respiration, in chimney-gases poor in CO_2, *&c.*

c. *Lindemann's Apparatus for estimating Oxygen*[*].

In a similar way oxygen can be estimated in many gaseous mixtures by means of moist phosphorus as absorbent. Other gases do not interfere, unless they are absorbed by water or unless they disturb the reaction between oxygen and phosphorus (comp. p. 49). Carbon dioxide in particular is all but indifferent in this case, a fact which is frequently of importance.

The apparatus is shown in fig. 35. 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 level-bottle C contains water, the absorbing-vessel B thin sticks of phosphorus and water up to the mark. The gas is introduced through the pinch-cock arrangement connected with the three-way cock; otherwise the manipulation is exactly as with Orsat's apparatus.

Application :—

a. *Estimation of oxygen in atmospheric air (whether containing*

* Modified by the author.

Fig. 35.
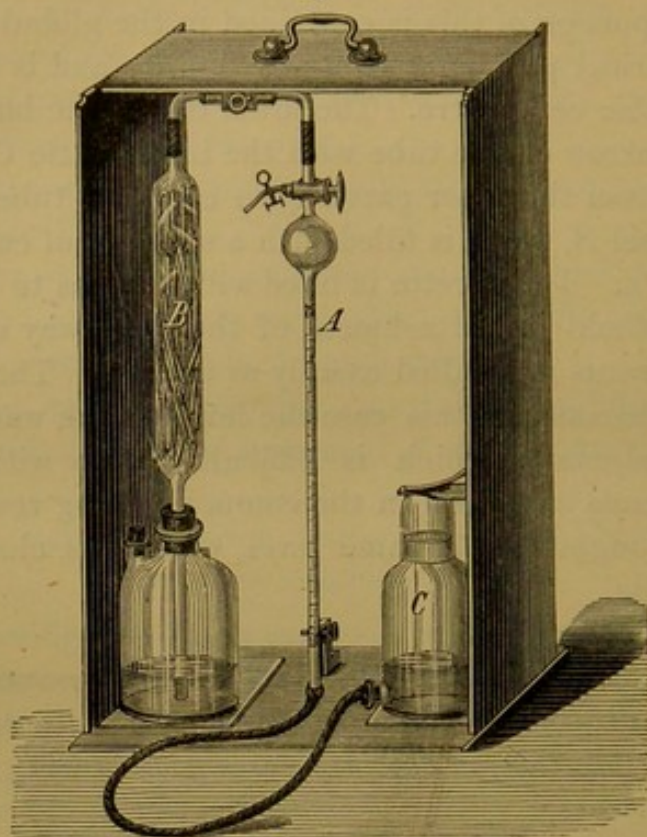
CO_2 *or not*) ; *in the air from graves, from respiration, Weldon's oxydizers, Bessemer converters, vitriol-chambers, &c.*

b. *Estimation of the proportion between oxygen and nitrogen in unabsorbed residues of gases,* such as are left on treating gaseous mixtures with alkaline liquids, for instance in gas from pyrites-kilns, from making sulphuric anhydride, from the Deacon process, &c.

d. *Hempel's Gas-burette.*

The measuring-tube A (fig. 36) has the same width throughout and contains exactly 100 c. c. from the zero mark at the bottom to the upper capillary end, which is closed by a pinch-cock or glass-rod arrangement. It is divided throughout into fifths of a cubic centimetre. The tube is perpendicularly cemented into a base made of thin cast iron, in such a way that its contracted end is carried out sideways at a right angle through this base. The level tube B, which is open at the top, possesses a similar base ; its bottom end is connected with that of the burette A by an india-rubber tube, which is conveniently interrupted in

the middle by a short piece of glass tubing, and which renders it possible to place the tube B at a higher or lower level.

By means of an interposed narrow glass capillary B, the burette A can be connected with the absorption-pipette C, also closed by a pinch-cock. This serves for submitting the gas, originally contained in the burette and transferred from the same,

Fig. 36.
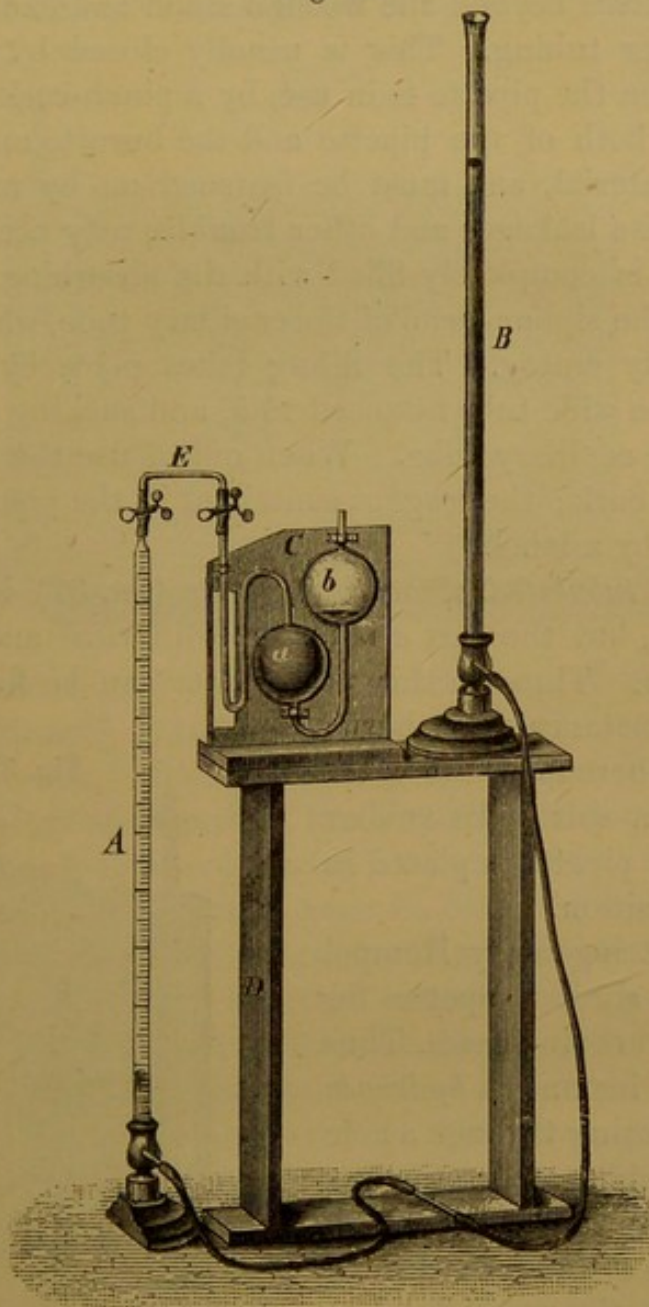
to the action of an absorbent. By a second, third, or fourth pipette, each of them filled with another liquid, one constituent of the gas after another can be removed, and its volume mea-

sured.   During this operation the pipettes are placed on the wooden stand *D*, whose height is so chosen that the outlets of the pipette are on a level with that of the burette.

The pipette shown in the diagram is what is called the *simple absorption-pipette*.   It consists of two glass bulbs *a* and *b*, fixed on a wooden stand and communicating by a bent tube.   The former of these is connected with a siphon-shaped capillary tube, projecting a few centimetres beyond the wooden stand and ending in a piece of india-rubber tubing.   This is usually closed by a short glass rod; but, when the pipette is in use, by a pinch-cock.   The india-rubber tubes both of the pipette and the burette must be of the best thick material, and must be fastened on by means of thin wire; otherwise leakages and other troubles may occur.

The bulb *a* is completely filled with the absorbing liquid, which reaches into the siphon-bend of the capillary tube, whilst the bulb *b* remains nearly empty.   The filling takes place by pouring the liquid into the wide tube attached to *b*, and sucking the air out of *a* through the capillary tube.   When out of use the open end of *b* is closed by a cork; the reagent contained in the pipette is marked on the stand by a label.

The simple tubulated absorption-pipette (fig. 37) is arranged in the same way, but the part *a* is made cylindrical and has a neck at the bottom.   Through this the pipette can be filled with solid reagents, for instance, phosphorus and water, whereupon the neck is closed by a soft india-rubber cork, and the pipette is placed in the proper position.

With great ingenuity Hempel has arranged similar pipettes for liberating and keeping gases. Thus we obtain, for instance, a *hydrogen pipette*, by passing through a hole in the india-rubber stopper a glass rod, tapering upwards, upon which is fixed a zinc cylinder perforated in the centre, the vessel *b* being filled with dilute sulphuric acid. As soon as the stopping of the capillary is taken away, the acid gets to the zinc and hydrogen is


Fig. 37.
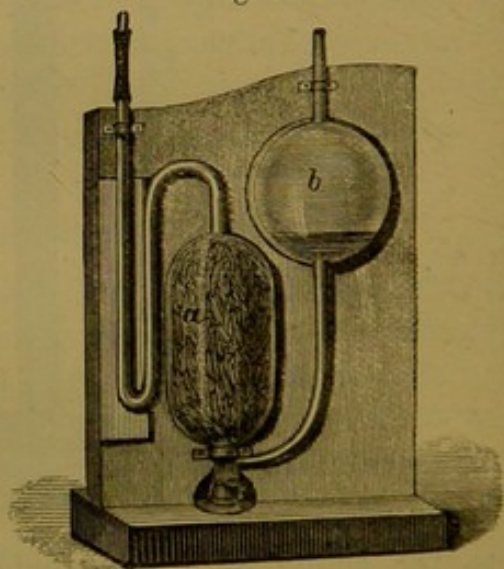
given off. This is allowed to continue till all air has been expelled ; on replacing the stopper the acid is forced back into the bulb *b* by the liberated gas and the evolution of hydrogen ceases, while a stock of the gas remains in the vessel *a*. In a similar way it would be possible to evolve carbon dioxide from marble and hydrochloric acid, or nitric oxide from copper and nitric acid.

The composite absorption-pipette (fig. 38) is used for keeping absorbents which suffer change in contact with atmospheric air,

Fig. 38.
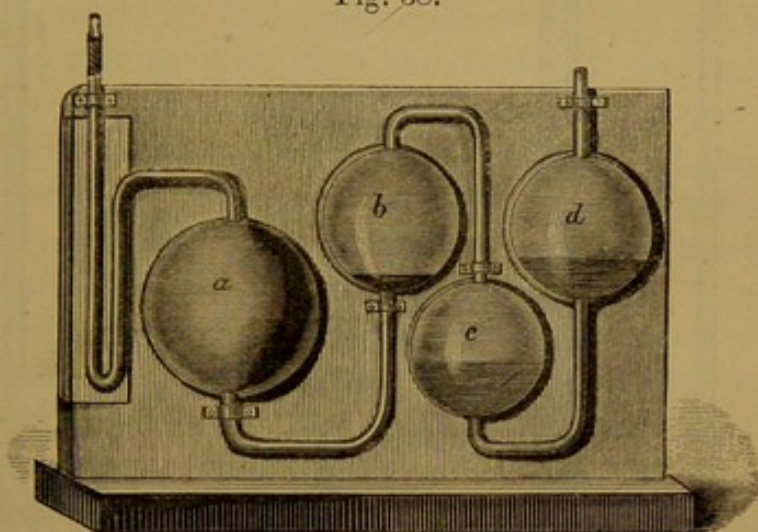
like alkaline solution of pyrogallol, or a solution of cuprous chloride in hydrochloric acid, or those which give off irritating vapours, such as bromine water. Here the pair of bulbs, *a* and *b*, forming the absorbing arrangement proper, are connected with a second pair of bulbs, *c* and *d*, which are converted into a water-joint by pouring in a little water. Such pipettes must be filled through the capillary tube fused on to the bulb *a*, by connecting its india-rubber end with a funnel-tube of about a metre in length (3 feet), through which the absorbing liquid is poured. If the liquid is to be filled through a short funnel, this can be done by attaching to the outer end of the bulb *d* an india-rubber tube with pinch-cock, and withdrawing the air contained in the apparatus by now and then sucking it out.

In order to render the measurements made with Hempel's burette as accurate as possible, and to keep the influence of the outer temperature away from its gaseous contents, the author has surrounded it with a wider glass tube, serving as a water-jacket. *Hempel's burette with water-jacket* is shown in fig. 39, and we need

only add that the outer tube is tightly fixed by india-rubber corks, and is provided at the top and bottom with small side-tubes,
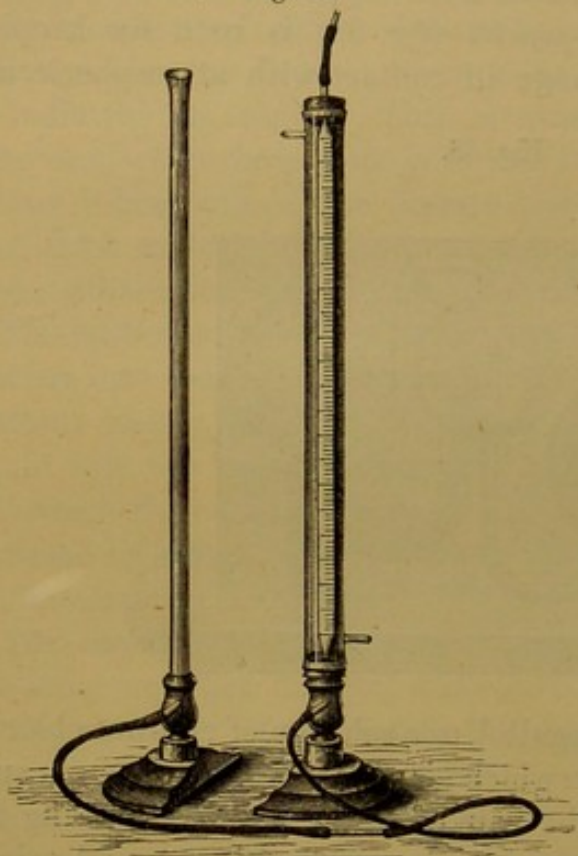
Fig. 40.

Fig. 39.
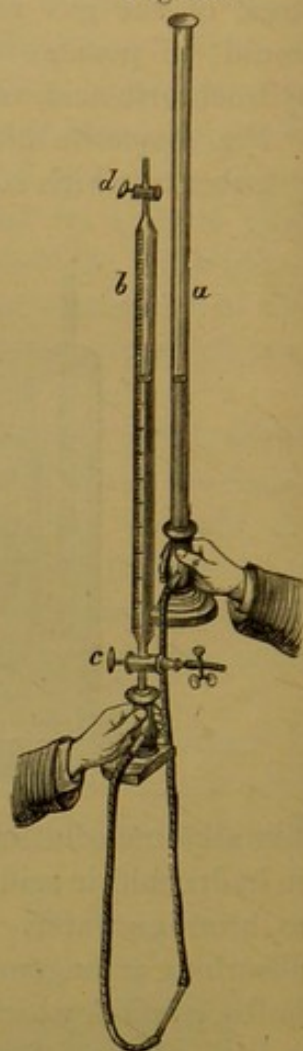
which serve for filling and emptying or for continuously running a stream of water of uniform temperature, and which are usually closed by small corks.

For the examination of gases which cannot be confined over water, on account of its too easy absorption of some of their constituents, Hempel uses what is known as the *modified Winkler's gas-burette* (fig. 40). This is closed at the bottom by a three-way cock *c*, and at the top by the simple glass tap *d* or by a pinch-cock ; the space between these contains 100 c. c., divided into fifths. Before introducing the gas the measuring-tube must be completely dried, which is conveniently done by rinsing it first with alcohol, then with ether, then blowing a rapid current of air through it. The filling is

effected by passing the gas through it until all air is driven out, for which purpose the pinch-cock attached to *c* is connected with the source of the gas, and the tap *d* with the aspirator, or *vice versá*. Otherwise the arrangement and manipulation are the same as with Hempel's burette.

Manipulation (comp. fig. 36).—Remove the connecting capillary tube *E*, lift up the level-tube *B*, previously filled with water, with the right hand, and with the left open the pinch-cock of the burette *A*, till it is full and the water begins to run out. Now connect the india-rubber end of the pinch-cock with the aspirating-tube, already filled with the gas, place the level-tube 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. of gas to enter, compress this by raising the level-tube till the water has risen in the burette above the zero mark, compress the connecting-tube close to the joint with the fingers, place the level-tube lower again, and by cautiously loosening the elastic tube, allow the water to run out until the zero mark has been just reached. Then, the connecting tube being still compressed, open for a moment the pinch-cock of the burette, so that the confined gas may be freed from the surplus pressure and assume that of the atmosphere. In this way it is possible to get exactly 100 c. c. of gas into the burette, as will be seen on bringing the water to the same level in both tubes. For exact measurements it is necessary to leave some time for the water to run down (p. 27); and in this case it is better not to employ exactly 100 c. c., but such a somewhat smaller volume as may be convenient.

When the gas has been measured, we proceed to absorb such of its constituents as are susceptible of the process. Connect the burette *A* by interposing the capillary tube *E* with the pipette *C*, move the pinch-cock up or down so as to leave the passage open, raise the level-tube with the right hand and at the same time open the pinch-cock of the pipette with the left hand. The gas now travels from the pipette into the bulb *a*, driving its liquid contents into the bulb *b*. When this has been accomplished, close both pinch-cocks and take the pipette off. Cause the absorption to proceed by gently moving the pipette about, or gently (not violently) shaking up its contents; the absorption is generally finished in about two minutes, but often much sooner, for instance, with carbon

dioxide. Now connect the pipette again with the capillary tube *E*, place the level-tube on the floor, and, by cautiously opening both pinch-cocks, make the gas re-enter the burette; the absorbing liquid should at last be just allowed admittance to the end limb of the capillary belonging to the pipette, but not to the connecting capillary, and still less to the burette itself. With some liquids inclined to frothing, such as the alkaline solution of pyrogallol, this cannot always be avoided ; if, in consequence of this, the india-rubber joints should become so slippery that the capillary tube will not hold fast, but slips off, the joints should be washed with water (the pinch-cocks being closed) and their ends moistened with a little dilute hydrochloric or acetic acid.

As soon as the water in the burette has closed up, the con-necting capillary is taken off, the level-tube is cautiously raised so high that both levels coincide (as in fig. 40, p. 56), and the reading is taken. In the same way a second, third, &c. con-stituent of the gas can be absorbed and estimated, each time employing a different pipette.

Application :—

a. *Estimation of carbon dioxide in mixtures of the same with air, or in gases of chimneys, blast-furnaces, lime-kilns, gas-producers, &c.,* employing a simple absorption-pipette, filled with concentrated solution of caustic potash.

b. *Estimation of oxygen in atmospheric air,* employing either a composite absorption-pipette, filled with a concentrated alkaline solution of pyrogallol, or a tubulated absorption-pipette filled with ammonia and small rolls of copper wire gauze, or (also in presence of carbon dioxide) a tubulated absorption-pipette filled with thin sticks of phosphorus and water.

c. *Estimation of ammonia, nitrous acid, nitric oxide, nitrous oxide, chlorine, hydrochloric acid, hydrogen sulphide, sulphur dioxide,* by employing a modified Winkler's burette and simple absorption-pipettes, to be filled for estimating :—

Ammonia . . . . . . with dilute sulphuric acid.

Nitrous acid . . . . with concentrated sulphuric acid, or with a solution of potassium permanganate acidu-lated with sulphuric acid.

Nitric oxide. . . . . with concentrated solution of ferrous sul-phate, or with potassium permanganate acidulated with sulphuric acid.

Nitrous oxide . . . . with alcohol.

Chlorine . . . . with solution of caustic potash.

Hydrochloric acid .   ,,   ,,   ,,

Hydrogen sulphide   ,,   ,,   ,,

Sulphur dioxide . . with solution of caustic potash, or solution of iodine.

d. Estimation of carbon dioxide, oxygen, and nitrogen in chimney or lime-kiln gases &c., by absorbing, that is to say, measuring one after another :—

1st, Carbon dioxide by solution of caustic potash.

2nd, Oxygen by alkaline pyrogallol, or copper and ammonia, or phosphorus and water.

3rd, Nitrogen as residue.

e. Estimation of carbon dioxide, oxygen, carbon monoxide, and nitrogen in chimney-, blast-furnace-, generator-gases, &c., by absorbing :—

1st, Carbon dioxide by solution of caustic potash.

2nd, Oxygen by alkaline pyrogallol, or copper and ammonia, or phosphorus and water.

3rd, Carbon monoxide by cuprous chloride and hydrochloric acid.

4th, Nitrogen as residue.

f. Estimating carbon dioxide, ethylene (propylene, butylene), benzene, oxygen, and carbon monoxide in illuminating gas, generator gas, &c., by absorbing :—

1st, Carbon monoxide by solution of caustic potash.

2nd, Ethylene (propylene, butylene) by bromine water, subsequently removing the vapour of bromine by employing the potash pipette.

3rd, Benzene by fuming nitric acid, subsequently removing the vapour of nitrogen peroxide by the potash pipette.

4th, Oxygen by alkaline pyrogallol, or copper and ammonia, or phosphorus and water.

5th, Carbon monoxide by cuprous chloride and hydrochloric acid.

6th, Hydrogen }
     Methane   remaining unabsorbed.
     Nitrogen

2. *Estimation by Titration.*

A. ESTIMATION BY TITRATION OF THE ABSORBABLE CONSTITUENT WITH MEASUREMENT OF THE TOTAL VOLUME OF THE GAS.

Hesse's Apparatus.

A conical absorption-bottle of strong white glass (fig. 41), holding from 500 to 600 c. c., or more or less, according to special requirements, is furnished with a mark in the neck, and is exactly measured up to this point; the volume is etched upon the glass. A doubly-perforated, tightly closing, india-rubber cork can be inserted to that mark, the perforations, unless closed by glass rods, serving to introduce inlet and outlet pipes, or the points of pipettes and burettes.

Fig. 41.

The standard solutions required, when working in the laboratory, are most conveniently measured by means of stationary burettes with inlet and outlet arrangement and floats (p. 35); for outdoor work they are carried in special bottles, as shown in fig. 42, which, according to circumstances, should be provided with guard - tubes &c., and the smaller of which can be easily replenished from the larger one by means of the siphon.

Manipulation.—In order to take the sample of gas the conical absorption-bottle is filled with water, a portion of which is then displaced by the gas to be examined, whereupon the india-rubber cork, already provided with its glass-rod stoppers, is put in and pressed down to the mark. If the employment of water must be avoided, for instance, in taking a sample of air contained in the soil, as shown in fig. 43, the india-rubber cork, provided with an inlet and an outlet tube, is put into the dry empty bottle, and the gas is drawn into it by means of a caoutchouc pump. When the
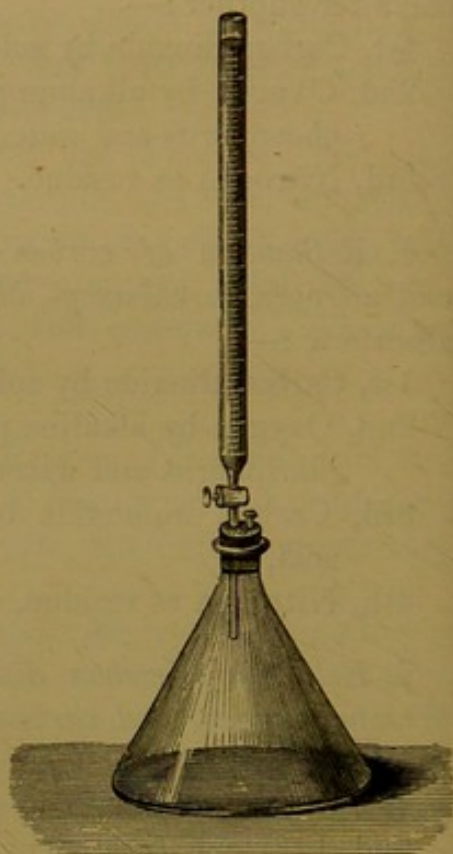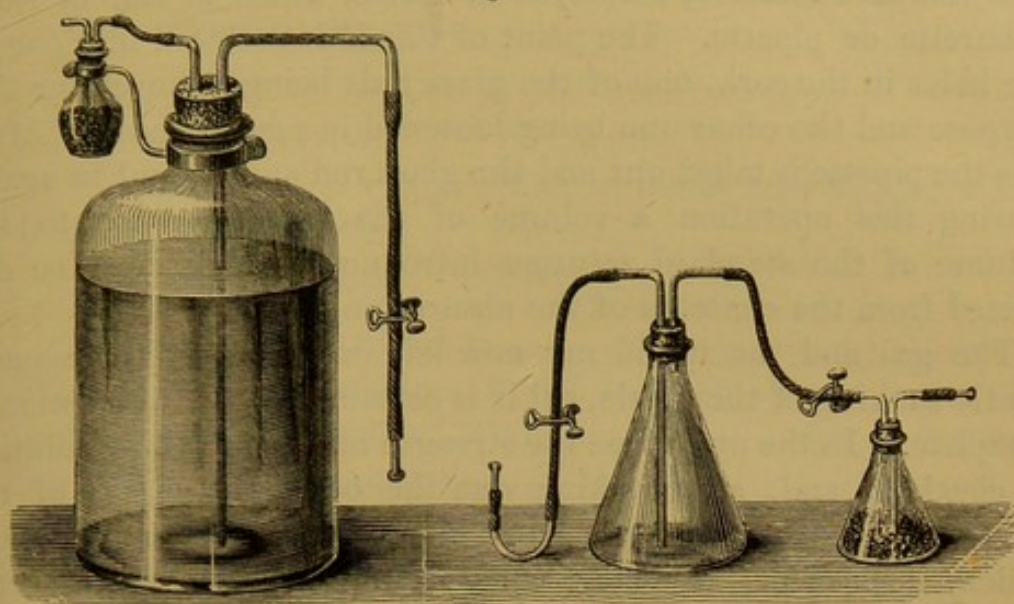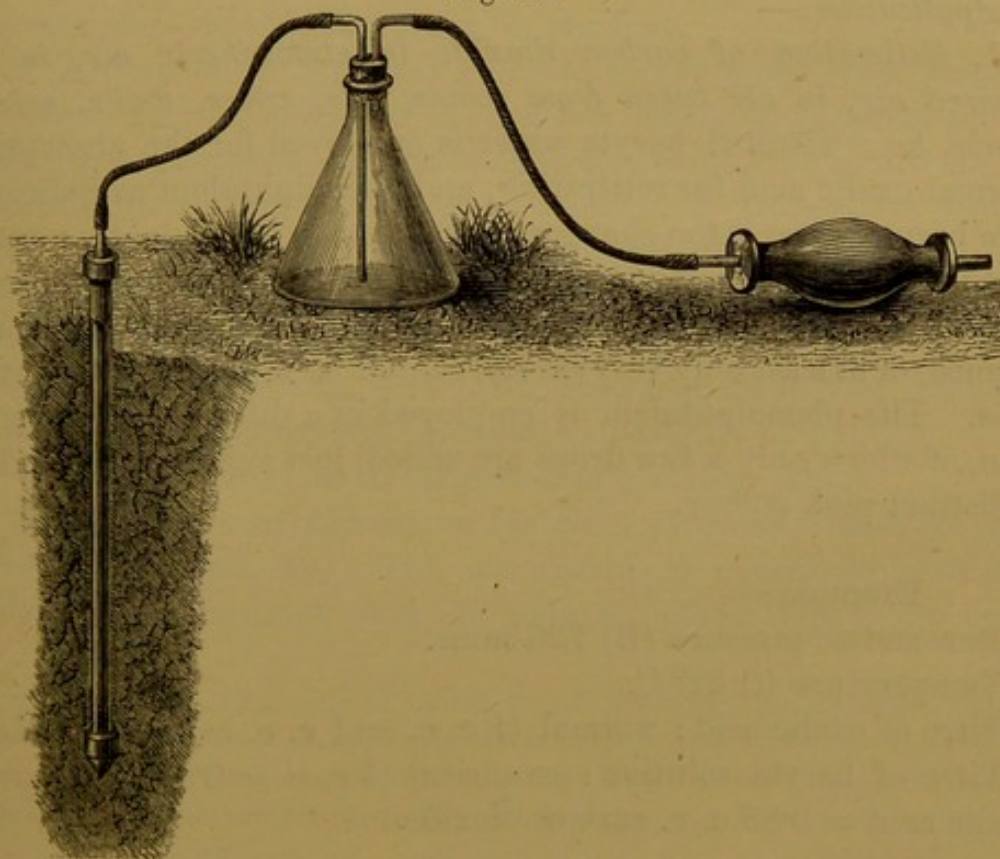
Fig. 42.

filling is complete, the end of the inlet pipe is drawn out of the cork, the hole in the latter is quickly closed by a glass rod, and the same is done with the smaller outlet pipe, turned towards the pump.

The absorbable constituent of the gas is now estimated by means

Fig. 43.

of a standard solution, employed in excess, which is run in from a burette or pipette. The point of this is introduced into one of the holes in the cork, one of the glass rods being removed for this purpose and the other one being loosened in case of need. After this the pipette is taken out and the glass rod quickly put in again. During this operation a volume of gas escapes, equal to the volume of the standard solution introduced, which must be deducted from the contents of the absorption-bottle.

The gas and the liquid are now left in contact, with frequent gentle shaking of the bottle, till it is certain that the absorption is complete. In the meantime the strength of the absorbing solution is checked, and, after taking out the cork, the excess of the absorbent is measured by means of a second standard solution, which, if possible, is made equal with the first, volume for volume. When employing normal solutions, the difference found corresponds to the volume of the absorbed constituent of the gas in cubic centimetres; and from this and from the total volume of gas employed the percentage is found by a simple calculation, not omitting the correction mentioned above.

This method is especially adapted for estimating small percentages, and yields satisfactory results.

Application :—

1. *Estimation of carbon dioxide in atmospheric air, in the expired air, in air taken from rooms, pits, caves, walls, subsoil, tombs, &c.* Titrated baryta water is employed for the absorption, normal oxalic acid for retitrating, and phenolphtalein as indicator. The baryta water is too changeable to be made permanently normal, and is therefore employed empirically, but approximately normal. Oxalic acid, which does not at all attack the barium carbonate formed, or at least only very slowly, cannot be replaced by any other acid. The phenolphtalein is employed in a dilute alcoholic solution, of which only a few drops are added, just sufficient to produce a distinct pink colour.

Example :—
Barometric pressure (B) 726 mms.
Temperature (*t*) 21° C.
Titre of oxalic acid : normal (1 c. c. = 1 c. c. carbon dioxide).
Titre of baryta solution : empirical (1 c. c. = 0·88 c. c. normal oxalic acid = 0·88 c. c. carbon dioxide).

Contents of absorption-bottle 618 c. c.
Baryta emyloyed 10 c. c.

Hence :—
Air employed 608 c. c.
10 c. c. baryta water require 8·8 c. c. oxalic acid and 1 c. c. CO_2.
Required for retitrating   6·0 c. c.   „   „
Difference   2·8 c. c.   „   „

Hence we have found in
608·0 c. c. air of 726 millims. B, 21° t, moist—
2·8 c. c. carbon dioxide of 760 millims. B, 0° t, dry or corrected.
525·5 c. c. air of 760 millims. B, 0° t, dry.
2·8 c. c. CO_2 „   „   „
Percentage found : 0·53 vols. CO_2 per cent.

In estimating very slight percentages, for instance, the carbon dioxide contained in normal atmospheric air, it is convenient to work with decinormal solutions. The amount of carbon dioxide is frequently expressed not in per cent., but in ten-thousandths. The air mentioned in the above-given example would have contained 53 ten-thousandths. It is also usual, and very properly so, to refer the percentage to a litre, that is, to express the amount in thousandths—in this case 5·3 c. c. per litre.

2. *Estimation of hydrogen chloride in the gases from salt-cake furnaces, hydrochloric-acid condensers, calcining furnaces for the extraction of copper by the wet process, &c.,* employing a normal silver solution for absorption, a normal solution of ammonium sulpho-cyanide for retitrating, and a solution of iron-alum as indicator. This process can also be modified in this way, that the hydrogen chloride is absorbed by a measured volume of solution of caustic potash, which is afterwards acidulated with nitric acid and titrated by Volhard's method, as just described (calculation like that of p. 62)*.

Cyanhydric acid can be estimated in a similar way.

3. *Estimation of chlorine in the gases from chlorine stills, from Deacon's process, &c.* The absorption is caused by a normal solution of arsenious acid in sodium bicarbonate ; the excess

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* When employing sodium carbonate as absorbent, the hydrogen chloride absorbed can be titrated by normal silver solution, potassium chromate serving as indicator. Even a considerable quantity of sodium carbonate in excess does not interfere with this reaction.—*Translator.*

employed is re-estimated by normal iodine solution, clear starch solution serving as indicator.

For estimating chlorine along with hydrogen chloride a second volume of gas is employed, a solution of arsenious acid in sodium carbonate being the absorbent; this is afterwards acidulated with nitric acid, and the total HCl—that is, that originally present in addition to that formed from the chlorine—is titrated as in No. 2, with silver solution and ammonium sulphocyanide *. In calculating it must be noted that each volume of chlorine produces two volumes of hydrogen chloride. Hence, in order to find the volume of the hydrogen chloride originally present, twice the volume of the free chlorine found must be deducted from the total volume of HCl †.

4. *Estimation of sulphur dioxide in the gases of pyrites, kilns, and chimneys, ultramarine furnaces, glass-houses, &c.* Absorption is produced by a solution of sodium carbonate of arbitrary, but not unnecessarily high strength; a little clear starch solution is added, and normal iodine solution run in till the blue colour appears (calculation as on p. 62).

B. Titration of the Absorbable Constituent, measuring the Unabsorbed Residue at the same time.

a. *Reich's Apparatus.*

The absorption takes place in the three-necked bottle A (fig. 44), which is filled to about half with the absorbing liquid through the middle neck, otherwise closed by a caoutchouc cork. One of the side necks is provided with the inlet pipe, drawn out to a point and bent at the end, and closed by the pinch-cock q; the other side neck serves for the outlet pipe, which is connected with the

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* Or without acidifying with silver solution, the silver arseniate serving as indicator.—*Translator.*

† In this case, as in the preceding No. 2, it is far more important to estimate the *weight* of HCl and Cl than the volume, both for practical purposes and to satisfy legal requirements. It is therefore preferable to deviate here from the rule otherwise observed in gas-analysis, by omitting the calculation into volumes of HCl and Cl respectively, and by employing, not the "normal" solutions otherwise meant in this book, *i. e.* such as indicate 1 c. c. of gas per 1 c. c. of the reagent, but the "decinormal" solutions of ordinary titration, or else solutions indicating per c. c. 0·001 grain, or parts of a grain, as the case may be.—*Translator.*

tin aspirator *B*.   Below the outlet pipe of the latter, closed with a tap *h*, a glass jar *C* is placed, which is divided into cubic centi-metres, and serves for holding and measuring to half a litre the water which runs out.
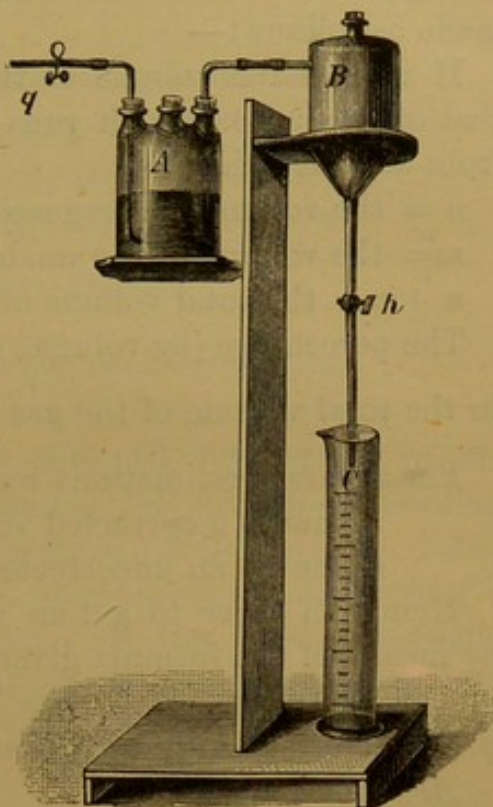
Manipulation.—Fill the ab-sorbing-vessel *A* rather more than half, the aspirator *B* entirely, with water, put all corks tightly in, close the pinch-cock *q*, and try whether the apparatus is quite tight. This is done by opening *h*; if the flow of water, continuous at first, soon changes into slow dropping, and at last ceases en-tirely, there is no leakage in the apparatus.

In order to test a gas, a suit-able volume of absorbing liquid is introduced into the vessel *A* by means of a pipette; if necessary, an indicator is also added, and the middle cork is again put in tightly.

Fig. 44.

The aspirating-pipe is now filled up to the pinch-cock *q* by means of a small india-rubber pump, and water is run off through the tap *h* till the liquid standing in the inlet pipe has just been forced down to its point, or until a single bubble of gas has issued. This is done in order to bring the air contained in the vessel *A* to the same pressure as that prevailing during the observation. The water which runs out is poured away, and the empty jar *C* is again put under the aspirator.

The measurement is effected by opening the pinch-cock *q* entirely, and afterwards the tap *h* so far that the gas is just aspirated. The gas is now passed through the vessel *A* in a slow stream, shaking from time to time, till the indicator shows that the reaction is finished.   At this moment both taps are closed, and the experiment is complete. Of course a second one may follow immediately, after adding a fresh quantity of the absorbent; the emptying, cleaning, and refilling of the vessel *A* need only be attended to at in-tervals.

F

The quantity of water run into the cylinder C is measured. Its volume is that of the unabsorbed residue of gas, that of the gaseous constituent absorbed following from the quantity and strength of the standard solution employed. This calculation is made as follows :—

If we call the volume of the employed normal solution n c. c., that of the water which runs out m c. c., there would be, apart from all corrections :—

$n =$ the volume of the gaseous constituent absorbed.

$m =$ the volume of the unabsorbed residue of gas.

$n + m =$ the total volume of gas employed for testing.

The percentage (by volume) of the constituent found by titration to the total volume of the gas tested would be $\dfrac{100 \times n}{n + m}$.

For accurate estimations we have to consider that

n means a corrected volume of gas ;

m means an uncorrected volume of gas.

Hence, in order to get an accurate result, m must be corrected by means of the formula given on p. 23, or by the table contained in the Appendix, or by the help of the apparatus described on p. 24, before making the calculation.

Applications :—

1. *Estimation of sulphur dioxide in pyrites kiln-gases.*—Add a little clear starch solution to the water contained in the absorbing-bottle, and by means of a pipette a suitable volume of normal iodine solution, and draw the gas to be tested through the liquid till the latter is only quite faintly blue. It is not convenient to decolorize the liquid entirely, because the experiment is thus very easily overdone ; should this be the case, the liquid must be coloured faintly blue by adding one or more drops of iodine solution before commencing a new test. Sometimes, especially when testing poor gases, it is advisable to add a little sodium bicarbonate to the absorbing liquid.

Example :—

Barometer (B), 732 millims.

Thermometer (t), 18° C.

Titre of the normal iodine solution ; 1 c. c. = 1 c. c. of sulphur dioxide.

Iodine solution employed (n) 25 c. c.

Water run out (m) 295 c. c.

The percentage of SO_2 will be found as follows :—

a. *Neglecting all corrections,* it is

$$\frac{100 \times n}{n+m} = \frac{100 \times 25}{25 + 295} = 7\cdot81 \text{ per cent. by volume.}$$

b. *Employing all corrections,* we have to consider that

$n = $ 25 c. c. at 760 millims. B, 0° t, dry.

$m = $ 295 c. c. at 732 millims. B, 18° t, moist, or

$m = $ 296·97 c. c. at 760 millims. B, 0° t, dry.

From this follows the corrected formula :—

$$\frac{100 \times n}{n+m} = \frac{100 \times 25}{25 + 260\cdot97} = 8\cdot74 \text{ per cent. by volume.}$$

c. *An approximate correction* is obtained by putting in the volume m as directly read off, but reducing the volume n according to the average pressure and temperature of the locality. For instance, at Freiberg, according to observations made during a year, 1 c. c. is in ordinary conditions on the average actually equal to 1·118 c. c. Hence we shall get an approximately correct result by putting into the formula the value $n \times 1\cdot118$ in lieu of n, thus :—

$$\frac{100 \times n}{n+m} = \frac{100 \times 25 \times 1\cdot118}{(25 \times 1\cdot118) + 295} = 8\cdot65 \text{ per cent.*}$$

2. *Estimation of nitrous acid in the gases of vitriol-chambers, Gay-Lussac columns, &c.*—The absorbent is a solution of potassium permanganate, which is made decinormal, as the amounts in question are only small. Before putting this into the absorbing-vessel, the latter is rather more than half filled with dilute sulphuric acid. The end of the reaction is shown by the decolorization of the liquid.

Example :—
Barometer (B), 728 millims.
Temperature (t), 22°.

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* It is evident that considerable errors may still remain when employing this "approximate" correction, unless at least the average temperature of the locality is replaced by that usually prevailing at the special place where the testing takes place, for instance the space close to the sampling-hole in the burner pipe.—*Translator.*

Titre of the potassium permanganate: 1 c. c. $= 0\cdot1$ c. c. N_2O_3.
Permanganate employed $2\cdot5$ c. c. ; $n = 0\cdot25$.
Water run out $(m) = 410$ c. c. ; or, corrected, $= 353\cdot61$ c. c.

Hence :—

$$\frac{100\,n}{n+m} = \frac{100 \times 0\cdot25}{0\cdot25 + 353\cdot61} = 0\cdot0706 \text{ per cent. by volume *.}$$

b. *R. A. Smith's Apparatus* (modified by the author).

The conical flask a (fig. 45) serves as absorbing-vessel; its contents, up to a mark in the neck, should be about 125 c. c., and should be measured exactly and etched upon the vessel. Its double-perforated caoutchouc stopper, which reaches down to the mark, carries an inlet pipe b, reaching down to the bottom, and an outlet pipe ending just below the stopper. The tube b is continued into a wider one, serving to receive a caoutchouc valve which opens only inwardly. Such a valve is made by sliding a bit of black, strong, elastic tubing on a smooth round piece of wood, and making in it a clean sharp longitudinal cut, about 2 centimetres long. The tubing is taken off from the wood, is closed at the bottom end with a piece of glass rod, and at the top with a glass tube open at both ends, which is carried through the perforated cork.

Fig. 45.

The tube c is connected with the pear-shaped india-rubber ball (finger-pump) d by means of about 30 centimetres of the best black, strong india-rubber tubing. This tube is also provided with a longitudinal slit of 2 centimetres, forming a valve which, when

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* In this case also it may be preferred to express the results in milligrams per litre, or the like, and to choose the standard liquids accordingly (comp. footnote to p. 64). Moreover it is for the most part not advisable to estimate the N_2O_3 by permanganate (comp. footnote to p. 74).—*Translator.*

the finger-pump is compressed, can only open outwardly, but which when the pressure is relaxed closes immediately and spontaneously. Consequently the compressed ball, when expanding owing to its elasticity, must receive the air necessary for its refilment through the valve *b*. Thus, by compressing the finger-pump with the hand, the air contained in it is forced out of the valve *c*, and by relaxing the pressure an equal volume of air is drawn through the valve *b* and through an absorbent contained in *a*.

The pump *d* serves not merely for pumping, but also as a measuring-apparatus. We choose for this purpose number 1 of the red English syringes, provided with a mouthpiece made of bone, such as are found at all shops selling surgical implements. Such syringes really hold 28 c. c. ; when compressing them with the hand, 23 c. c. are pretty constantly forced out each time. Hence on testing a gas it is only necessary to count the number of times of working the pump, and to multiply this by 23, in order to learn the volume of the aspirated gas, minus that retained by the absorbing liquid.

Manipulation.—The tube *b* is connected by elastic tubing with the place from which the gas is to be taken, or else the observer takes the apparatus directly into the atmosphere to be tested, and, first by eight or ten compressions of the pump, completely fills the apparatus with the gas in question. The cork is raised for a moment, and a known volume of absorbing liquid is put into the vessel *a*, along with an indicator, if necessary, whereupon the cork is again firmly pressed into the neck of the flask. The volume of the absorbing liquid employed must be deducted from the volume of gas contained in the flask *a* at the commencement of testing. The gas is now gently shaken up with the liquid, but without wetting the upper part of the flask or the cork ; then the finger-pump is compressed to aspirate another volume of gas, the liquid is shaken up again, the pump is compressed again, and this is continued, always counting the workings of the pump, till the indicator shows the end of the reaction.

The result is calculated in the same way as indicated for Reich's apparatus, but leaving out all corrections, as this method can in no case claim more than an approximate degree of exactness.

If $n =$ the volume of the gas absorbed ($=$ the volume of normal solution employed) ;

$m =$ the volume of the unabsorbed gas (equal to the contents

of the absorbing-vessel, less the volume of the absorbing liquid, but adding the number of workings of the pump, multiplied by 23);

$n + m =$ the total volume of gas tested;

the gas contains $\dfrac{100 \times n}{n+m}$ per cent. by volume of the absorbable constituent.

This method is best adapted for the rapid, if only approximate, estimation of small percentages. The apparatus is compact, simple, and cheap. Its employment for what is known as the minimetrical method of estimation (for which it was originally designed by Dr. R. A. Smith, and introduced into Germany by the Translator in a somewhat modified form)—in which the final reaction consists in producing a certain degree of turbidity within the absorbing liquid—cannot be recommended, as the degree of accuracy obtained in this manner is quite insufficient.

Applications :—

1. *Estimation of carbon dioxide in atmospheric air, in expired air, in the air of rooms, coal-pits, caves, walls, subsoil, tombs, &c.*, employing titrated baryta-water for absorption and phenolphtalein as indicator. An alcoholic solution of the latter is added in only just sufficient proportion to produce a distinct pink colour. After each working of the finger-pump the flask should be shaken for 25 or 30 seconds; otherwise the absorption is incomplete.

Example :—

Titre of the baryta-water empirical, but approximately decinormal; 1 c. c. $=0\cdot 104$ c. c. carbon dioxide.

Total contents of the absorbing-bottle 128 c. c.

Baryta-water employed 25 c. c. ; $n = 0\cdot 104 \times 25 = 2\cdot 60$ c. c. CO_2.

Air contained in the absorbing-bottle $128 - 25 = 103$ c. c.

Required for decolorization : 19 syringes full at 23 c. c. each $= 437$; hence $m = 540$ c. c., or $\dfrac{100 \times n}{n+m} = \dfrac{100 \times 2\cdot 6}{2\cdot 6 + 540} = 0\cdot 47$ per cent. by volume.

2. *Estimation of hydrogen chloride in the air of alkali-works, in the flues and chimneys of salt-cake furnaces, in the gases from copper-calcining furnaces, &c.*, employing normal solution of caustic potash as absorbent and a little methyl-orange as indicator. The end of the reaction is shown by the colour changing from light yellow into pink. When testing air very poor in HCl,

employ a decinormal solution.   Manipulation and calculation as
in No. 1.

3. *Estimation of sulphur dioxide in dilute burner-gas, chimney-
gas, metal-smelting gases, &c.,* employing normal iodine solution
as absorbent.   An addition of clear starch-solution is convenient
but not indispensable.   The absorption takes place easily and
quickly, without long shaking.   Calculation as in No. 1.

c. *Apparatus for Estimating Single Constituents occurring in Minute Quantities.*

The tap *a* (fig. 46) forms the connection with the place from
which the gas is taken.   The *aspirator d* serves as aspirating
and at the same time mea-
suring apparatus; its upper
tap, in case of need, can be
provided with a micrometer
screw for facilitating its re-
gulation.   The contents of
the aspirator, which is com-
pletely filled for each experi-
ment, are known once for
all; at each measurement all
the water is run out, and its
volume is accordingly equal
to that of the unabsorbed
gaseous constituent.   In
lieu of the aspirator we may
employ a *gas-meter,* con-
nected with some aspirating
arrangement behind; but
in both cases care must be
taken that the diminution
of pressure in the aspirating
and measuring apparatus
should be but slight, just
sufficient to cause the gas to
pass through the absorbing
liquid.   The error caused
by this can be lessened by

Fig. 46.
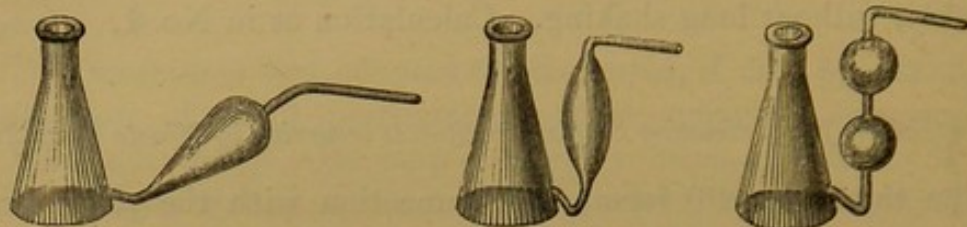
arranging that the water does not run out freely from the point
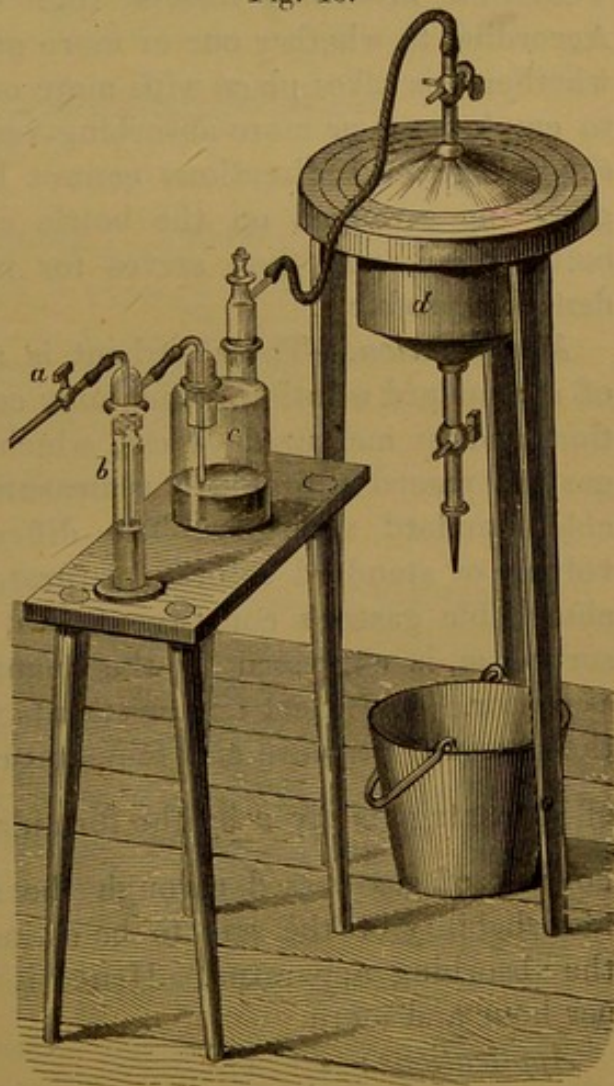
of the aspirator, but through an elastic tube, ending in a glass tube dipping under water.

Between the tap a and the aspirator d the absorbing-vessels are interposed, which may have the shape shown in b and c, or any

Fig. 47.

other suitable form. Where it is afterwards necessary to titrate, Volhard's absorbing-vessels (fig. 47) can be recommended. According to whether one or more gases are to be absorbed, and whether this takes place with more or less difficulty, we shall have to employ one or more absorbing-vessels of equal or of differing shapes; general directions cannot be given on this point. The glass top arranged on the bottle c can be loosely filled with cotton wool, and then serves for retaining tarry or other condensable products.

Manipulation.—The absorbent is always employed in the shape of a standard solution, which may conveniently be a normal solution, and in measured excess, which, after a certain quantity of gas has passed through, is remeasured by means of another suitable standard solution. The difference, corresponding to the volume of standard solution saturated, shows the volume of the absorbable gaseous constituent $=n$, while that which is not absorbed, m, is expressed by the quantity of water run out of the aspirator. For exact measurements the latter must be reduced to the standard pressure and temperature; otherwise the calculation of percentage is given by the formula $\dfrac{100\,n}{n+m}$. The velocity of the current of gas passed through the absorbent is adapted to the absorbability of the gas to be estimated, and to the capacity of the absorbing apparatus. Hence it may vary from 1 to 20 litres per hour and more.

Applications :—

1. *Estimation of ammonia in raw or purified illuminating gas, in the gases from coke-ovens, from ammonia-soda works, &c.*—The

absorbent is normal sulphuric acid, which is retitrated with normal solution of potash; as indicator we employ tincture of cochineal or hematoxylene*. The measured absorbing liquid is put in the cylinder b (fig. 46), and, for testing illuminating gas, c is charged with a solution of lead acetate to retain the hydrogen sulphide present. If tar is also present, the gas before entering the aspirator is passed through cotton-wool contained in the top part of c. For estimating the ammonia contained in crude illuminating-gas and in coke-oven gases, 20 litres, or for purified illuminating-gas 100 litres, of gas is a sufficient quantity to be tested. In the latter case a gas-meter with an automatic shut-off arrangement (p. 31) is most convenient. Since the ammonia is very easily absorbed by the acid, the gas may be passed through rapidly, say from 15 to 20 litres per hour.

Example :—

Estimation of ammonia in purified illuminating-gas.
Barometer (B), 730 millims.
Temperature (t), 18° C.
Normal sulphuric acid employed . . . 20·00 c. c.
Normal potash solution used . . . . . 17·38 ,,
Difference (n) . . . . 2·62 ,,
Gas passed through the meter (m), 100 litres.
The same, corrected volume, 88,216 c. c.

Percentage of ammonia following from these data :—
a. Neglecting corrections :
$$\frac{100\,n}{n+m} = \frac{100 \times 2 \cdot 62}{2 \cdot 62 + 100,000} = 0 \cdot 00262 \text{ per cent. by volume.}$$
b. Employing the corrections :
$$\frac{100\,n}{n+m} = \frac{100 \times 2 \cdot 62}{2 \cdot 62 + 88,216} = 0 \cdot 00297 \text{ per cent. by volume.}$$

Such small amounts are not usually expressed in per cent. by volume, but in grammes per 100 litres of gas. The gas in question would have contained 2·26 grammes NH_3 in 100 litres.

2. *Estimation of nitrous acid, chlorine, hydrogen chloride, sulphur dioxide.*—A suitable volume of gas is passed through the absorbent,

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* As to the employment of "normal" solutions, where the weight and not the volume of the absorbable gas is sought, both in this and the following cases comp. the footnote, p. 64. As indicator, methyl-orange does very good service. —*Translator.*

employed in excess, and the quantity taken up is found either by direct titration, or by remeasuring the excess of absorbent by means of a suitable standard liquid.

a. *Nitrous acid.*—The absorbent is concentrated sulphuric acid. Employ a suitable quantity of this; after finishing the absorption take out a portion by means of a pipette, run it out into a large quantity of cold water, and titrate with potassium permanganate *.

b. *Chlorine.*—The absorption is made by means of any given quantity of concentrated solution of potassium iodide, which, however, in any case must be more than sufficient; in case of need sodium bicarbonate is added in order to saturate any free acid absorbed, and the liberated iodine is titrated by arsenious acid.

c. *Hydrogen chloride.*—The absorption is made by a known volume of normal solution of potash, and the excess remeasured by normal acid. Where other gaseous acids are present at the same time, the absorbing liquid, at the end of the operation, may be saturated with nitric acid, whereupon a measured excess of normal silver solution and a little iron-alum solution is added, and the excess of silver retitrated with ammonium sulphocyanide (comp. p. 63 and the footnote on p. 64).

d. *Sulphur dioxide.*—The absorbent is a known volume of normal iodine solution, the excess being retitrated with arsenious acid.

In all these cases the calculation is made as for ammonia (p. 73).

3. *Estimation by Weight.*

The estimation of gases by converting them into compounds capable of being weighed is only made in exceptional cases, especially those in which the constituent to be estimated is present in very slight quantity, and where volumetric methods cannot be employed. The construction and manipulation of the absorbing-

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* Since in most cases where nitrous acid (nitrogen trioxide) is to be estimated, the presence of either nitrogen peroxide or of nitric oxide (N_2O_4 or NO) is to be taken into account as possible, the process described in the text cannot be recommended, because it does not indicate the real quantity of nitrogen compounds present, and may lead to considerable errors. It should hence be combined with estimating the total nitrogen compounds, *e. g.* by means of Lunge's nitrometer, described p. 96. In many cases the latter estimation alone is quite sufficient.—*Translator.*

apparatus are the same as described on p. 71, and the calculation of the results is generally made in the same way as is there indicated.

Application :—

Estimation of hydrogen sulphide, carbon disulphide, and acetylene in illuminating gas.—The current of gas, to be measured by a meter or an aspirator, before entering these passes through two Volhard's absorbing-apparatus (fig. 47), each of them containing 20 c. c. of a concentrated ammoniacal solution of silver nitrate, then through a combustion-tube of about 25 centimetres length, filled with platinized asbestos * and heated to an incipient dark red ; finally, again with two Volhard's apparatus containing 20 c. c. of ammoniacal silver solution each. For greater security three absorbing-vessels may be employed before and behind the combustion-tube, in lieu of two. For each test 100 litres of gas should be employed, and 10 to 12 hours should be allowed for passing them through.

The contents of the two receivers placed in front of the combustion-tube after some time assume first a whitish, then a darker turbidity, caused by the precipitation of silver acetylide and sulphide. These receivers absorb the acetylene and the hydrogen sulphide.

Carbon disulphide and other sulphur compounds present in coal gas, on passing through the combustion-tube and coming in contact with the hot platinized asbestos, are changed into hydrogen sulphide, which is absorbed in the following receivers, and causes a blackish-brown precipitate of silver sulphide.

After finishing the operation, the contents of the two first receivers on the one hand, and those of the two last receivers on the other hand, are united ; each of the two precipitates is filtered and carefully washed with water. The precipitate originally contained in the first receivers is covered on the filter with dilute hydrochloric acid, which process must be performed cautiously, keeping the funnel covered with a watch-glass. Acetylene is given off with slight effervescence, the precipitate being converted into a mixture of silver chloride and silver sulphide. After washing it, the silver chloride is extracted by a little dilute ammonia, re-precipitated by saturating the filtrate with nitric acid, and weighed in

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* See the preparation of this later on (p. 77).

the usual manner. From the weight of this precipitate that of the *acetylene* may be deduced by means of the formula :—

$$(C_2Ag_2H)_2O + 4HCl = 4AgCl + 2C_2H_2 + H_2O.$$
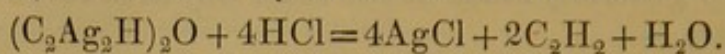
1 gramme AgCl corresponds to 0·09068 gramme acetylene = 78·0314 c. c. in the normal state.

The silver sulphide, which is insoluble in ammonia and has remained on the filter, corresponds to the *hydrogen sulphide* originally present. Examination has proved that it contains no free silver; hence the precipitate, after burning the filter, can be at once converted into metallic silver by igniting in a current of hydrogen.

1 gramme of silver corresponds to 0·148522 gramme S, or 0·157811 gramme H_2S, or 103·6661 c. c. H_2S in the normal state.

The silver sulphide found in the receivers placed behind the combustion-tube has been produced from the other sulphur compounds present in illuminating gas, as *carbon disulphide, phenyl sulphocyanide,* &c. It is converted in the same way into metallic silver, which is weighed and calculated as carbon disulphide, which is the predominant compound. 1 gr. of silver corresponds to 0·148523 gr. S, or 0·176319 gr. CS_2, or 51·8326 c. c. CS_2 in the form of gas in the normal state.

It is not usual to express the percentage of H_2S and CS_2 in coal-gas by volumes, or as weights of these compounds, but merely to indicate the number of grammes of sulphur contained in 100 cubic metres of gas (in England in grains per cubic foot), that is *the total sulphur contained in the illuminating gas.* Since, moreover, the gases in question occur in coal gas only in minute quantities, their volumes need not be counted when calculating the results, the unabsorbed gas measured in the meter or aspirator being put equal to the total volume of gas tested.

Example :—
Barometer (B), 733 millims.
Temperature (*t*), 18° C.
Volume of gas employed, 107 litres.
The same corrected, 94,787 c. c.

Found by weighing :—
AgCl = 0·3190 gr. = 24·78 c. c. acetylene.
Ag *a* = 0·0111 gr. = 1·15 „ hydrogen sulphide.
Ag *b* = 0·3888 gr. = 20·15 „ carbon disulphide.

Total sulphur :—
Silver $a = 0\cdot0111$ gr. $= 0\cdot001648$ gr. S.
   ,, $b = 0\cdot3888$,, $= 0\cdot057746$,,
100 cubic metres of gas contain $62\cdot66$ grammes sulphur*.

Expressed in per cent. by volume :—
Acetylene . . . . . $0\cdot02614$ p. c.
Hydrogen sulphide $0\cdot00121$,,
Carbon disulphide $0\cdot02126$,,

II. Estimation of Gases by Combustion.

1. *Combustion of Gases with the aid of Air and Palladium-asbestos.*

A. Hempel's Gas-pipette, with Capillary Combustion-Tube.

This extremely simple 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 palladium, has been loosely introduced, so that it does not impede the passage of a current of gas.

Palladium-asbestos is prepared in the following way :—Dissolve 1 gramme palladium in aqua regia, evaporate the solution to dryness on a water-bath, so as to remove any adhering hydrogen chloride as completely as possible, and dissolve the palladium chloride thus produced in a very little water. To this add a few cubic centimetres of a cold saturated solution of sodium formiate and sufficient sodium carbonate to produce a strongly alkaline reaction. Now introduce 1 gramme of very soft, long-fibred asbestos, which, if any unnecessary excess of water has been avoided, absorbs the whole liquid and forms with it 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, the asbestos thus prepared must be heated on a water-bath till completely dry, then soaked in a little warm water, put into a glass funnel and freed from all adhering salts by thorough washing, without removing any palladium. After drying, the substance exhibits a dark grey colour, having a slight tendency to stain the fingers, and contains 50 per cent. palla-

* 1 gramme per cubic metre $= 0\cdot44$ grain per cubic foot.—*Translator*.

dium. It possesses a very high degree of chemical activity; in the perfectly dry state it can cause the combination of hydrogen and oxygen even at the ordinary temperature, but in order to secure this result it is always employed in the heated state. The same process is employed for producing *platinum-asbestos*, required for other purposes (p. 75), but it is sufficient to make this with from 10 to 25 per cent. of platinum.

For the preparation of the capillary combustion-tubes we employ capillary glass-tubing of about 1 millim. bore and 5 millim. outside diameter, cut in pieces 15 or 16 centimetres long. The asbestos-fibre must be introduced into them before bending off the end, 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 centimetres; they are moistened with a few drops of water, and, by sliding the finger over them, are twisted into a fine straight thread, which in the moist state has the thickness of stout sewing-cotton. This thread is grasped at one end with the nippers, and, without bending or nicking, is slid from above into the capillary tube, which is held vertically. This is then filled with water by means of the washing-bottle, and by jerking or by drawing off the water at the ends the asbestos-thread is brought into the centre of the tube. This is now allowed to dry in a warm place; the two ends are bent off at right angles for a length of 3·5 or 4 centimetres, and the edges rounded off with the lamp.

The *measuring-apparatus* (fig. 48) is a Hempel's burette, *A*, with a simple absorbing-pipette, *C*. The latter is filled with water and has a brass tube, *g*, fixed to the back of the stand, but movable in different directions and ending in a small steatite burner. This tube is connected with the gas-supply by an elastic tube, and serves for producing a small gas-flame, *F**. By means of this, the capillary combustion-tube *E*, placed between *A* and *C*, can be heated at will; if the heating is to be interrupted, the flame need not be put out, but the tube *b* need only be moved a little backwards.

Manipulation.—The volume of the combustible gas contained in the burette *A* is read off; it should in no case exceed 25 c. c. The level-tube is placed on the floor of the room, and by opening the pinch-cock, enough air is admitted to bring up the total volume

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* Of course this gas-jet may be conveniently replaced by the small spirit-lamp attached to Lunge-Orsat's apparatus, fig. 49.—*Translator.*

Fig. 48.
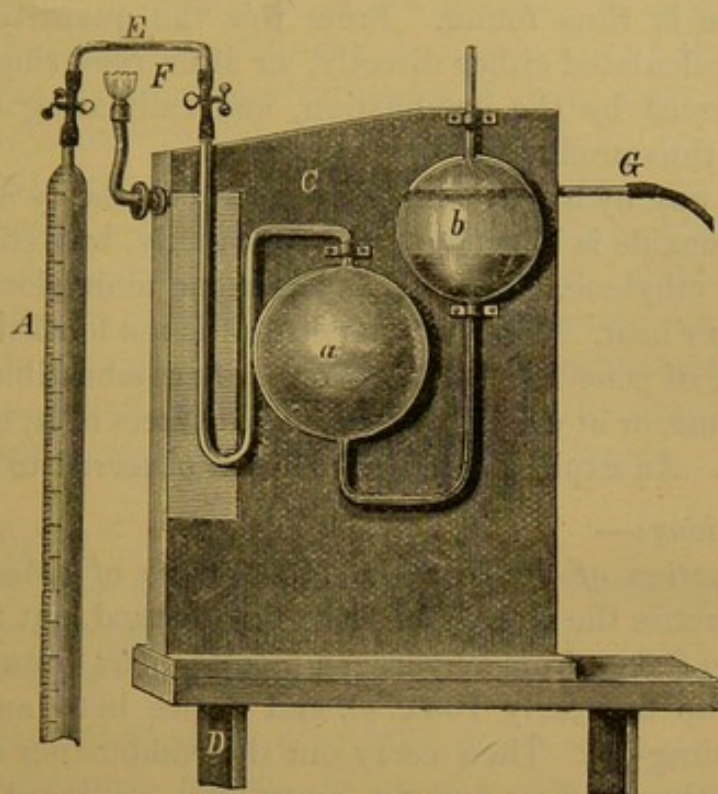
of the confined gases nearly, but not quite, to 100 c. c.   When
all the water has run together, the volume is carefully read off.
The capillary tube E is now interposed between the burette A and
the pipette C, and heated for one or two minutes by means of the
small gas-jet F.   The heating should be only slight, and should in
no case rise till the tube is at a visible red heat, still less till it
softens.   The combustion may now begin.   The level-tube is ele-
vated, the pinch-cocks are opened, and the gaseous mixture is con-
veyed in a slow stream through the heated palladium-asbestos into
the pipette C.   The end of the asbestos-thread first meeting the
gaseous current begins to glow visibly, and this glowing frequently
reappears when conveying the gas back into the burette in the
same way.   During the whole operation the gas-jet is left burning
under the capillary tube; otherwise care must be taken lest the
gas should pass too quickly and lest any drops of water should get
into the heated part of the capillary tube, which would thereby be
sure to crack.   With easily combustible gases, the combustion is
usually finished by two passages forward and backward; but in
any case it is necessary to be convinced that no further decrease
of volume takes place by another passage.   The residue of gas

ultimately obtained is measured; and the contraction which has taken place is thus found. From this the quantity of the gas burned is calculated either directly, or after removing any carbon dioxide formed by the combustion, and estimating the decrease of volume thus produced.

In this way hydrogen can be burned most easily and quickly; carbon monoxide is burned a little less easily, but still quite conveniently; ethylene, acetylene, and benzene more slowly, and only at a stronger heat. Methane (marsh-gas) is not burned at all; even in presence of considerable excess of easily combustible gases there is no methane, or at most extremely slight traces of it, burned along with them. An explosion has never been observed to take place.

Applications :—

1. *Estimation of hydrogen in the absence of other gases.*—In order to practise the manipulation of this method, put 20 or 25 c. c. of hydrogen (taken from a hydrogen pipette, p. 54) into the burette, admit air up to nearly 100 c. c., and notice both amounts after careful reading-off. Then carry out the combustion as described, and by another reading find the contraction produced. The combustion takes place according to the equation :—

$$2H + O = H_2O.$$
$$2 \text{ vols.} + 1 \text{ vol.} = 2 \text{ vols.}$$
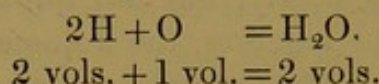
Since the water produced is condensed, there is 1 vol. of oxygen abstracted for each 2 vols. of hydrogen; and thus the volume of the hydrogen originally present is found on multiplying the contraction observed by two thirds. Since the hydrogen employed is never quite pure, the yield will be always a little deficient.

Example :—

Hydrogen employed . . . . =22·8 c. c.
Hydrogen + air . . . . =98·0 „
Hence air alone . . . . =75·2 „
Oxygen contained in the same. . =16·3 „
Oxygen required by theory . . . =11·4 „
Excess of oxygen employed . . . = 4·9 „
Volume of gas after combustion . =64·0 „
Contraction . . . . =34·0 „

Found :—

$$\frac{34 \times 2}{2} = 22·66 \text{ c. c. hydrogen.}$$

2. *Estimation of hydrogen in the presence of other gases*, for instance *in water-gas, heating-gas, coal-gas.*—The following gases, if present, are removed and estimated first by absorption, in the order given : carbon dioxide, ethylene (propylene, butylene), benzene, oxygen, carbon monoxide (see p. 59) ; the remaining gas or a measured portion of it is mixed with a quantity of air, sufficient in any case for burning the hydrogen present, and the mixture passed over heated palladium-asbestos. The gaseous mixture now left can only contain, as belonging to the original gas, methane and nitrogen, mixed with the remainder of the atmospheric air, that is nitrogen and oxygen, whose volume is known.

Example :—

Estimation of a heating-gas containing nitrogen, produced by working coke-gas producers with air and steam.

Volume of gas employed, 97·7 c. c.

A. *Estimation of the absorbable gases.*

After absorption by potash   87·5 c. c.

Decrease of volume . . .	12·0	,,	$= 12\cdot8$ volume p. c. CO_2.

After absorption by cuprous chloride . . . . } 68·6 ,,

Decrease of volume . . .	17·1	,,	$= 17\cdot46$ p. c. CO.

Unabsorbed residue . . . . 68·6 ,,

B. *Estimation of hydrogen.*

Since the volume of the non-absorbable gaseous residue is too large to admit of the admixture of a sufficient quantity of air for burning the hydrogen within the confined space of the burette, only a portion of it is employed for continuing the analysis.

Unabsorbed gas employed (equal to 86·44 per cent. of the original volume of gas) . . . . } 59·3 c. c.

Gas + air	98·8	,,
Air alone	39·5	,,
In this : Oxygen	8·2	,,
Nitrogen	31·3	,,
Volume after combustion .	80·5	,,
Contraction	18·3	,,

Corresponding to :—

Hydrogen (from the original mixture) . . . . } 12·2 c. c. = 14·43 per cent. by volume.

Oxygen (from the air) . . . 6·1 „

Noncombustible residue . . 80·5 „

C. *Estimation of nitrogen.*

The amount of nitrogen in the gas is found by deducting from the noncombustible residue that which was left from the air employed for combustion.

Noncombustible residue . . . . 80·5 c. c.
Containing oxygen of the air (8·2 — 6·1) = 2·1
  „   nitrogen   „   „   31·3
                      ———
   Altogether . . . . 33·4 c. c.
The difference is nitrogen . . . . 47·1 „ = 55·77 per cent. by volume.

Final result :—

Carbon dioxide . . . . 12·28
Carbon monoxide . . . . 17·46
Hydrogen . . . . 14·43
Nitrogen . . . . 55·77
                ———
                99·94

3. *Estimation of oxygen in atmospheric air and other suitable mixtures of gases.*—Add to the gas measured off in the burette a volume of hydrogen exceeding twice the possible percentage of oxygen, and let the combustion take place in the capillary tube. Since two volumes of hydrogen vanish for each volume of oxygen, the contraction observed, divided by 3, yields the proportion of oxygen.

Example :—

Air employed . . . . 66·7 c. c.
Air + hydrogen . . . . 99·2 „
Hydrogen added . . . . 32·5 „
Hydrogen required by theory . . . 27·6 „
Hydrogen in excess . . . . 4·9 „
Volume after combustion . . . . . 57·8 „
Contraction . . . . 41·4 „

Found :—

$$\frac{41\cdot4}{3} = 13\cdot8 \text{ c. c.} = 20\cdot69 \text{ per cent. by volume of oxygen.}$$

4. *Estimation of carbon monoxide in chimney-gases, blast-furnace gases, fire-damp, &c.*—The carbon dioxide is first estimated by absorption, a measured excess of air is then added to the unabsorbed residue, or to a measured portion of it, and the combustion is made by the capillary tube. The equation is

$$CO + O \quad = CO_2,$$
$$2 \text{ vol.} + 1 \text{ vol.} = 2 \text{ vol.} ;$$
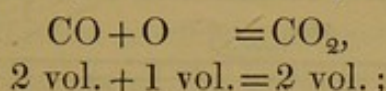
hence the volume of the air to be added must be at least $2\frac{1}{2}$ times that of the carbon monoxide present. The contraction taking place after the combustion must be multiplied by 2 ; but it is more accurate to absorb the CO_2 produced by combustion in the potash pipette, and to multiply the total decrease of volume by $\frac{2}{3}$.

The combustion of carbon monoxide to carbon dioxide by means of palladium- (or platinum-) asbestos is especially useful for estimating very slight quantities of carbon monoxide, such as may occur in the air of inhabited rooms, or (frequently along with marsh-gas) in the "fire-damp" of coal-pits. But in this case the carbon dioxide cannot be estimated volumetrically, but must be titrated. For this purpose we employ the apparatus described and figured for the estimation of methane (see below, fig. 50); but, in lieu of the combustion-tube charged with copper oxide, a tube of equal size, charged with platinum-asbestos, is employed, and heated just to an incipient red heat. In this case carbon monoxide only, and no methane, is burned. The CO_2 formed is absorbed by titrated baryta-water (as in the case quoted), and the excess of the latter retitrated with normal oxalic acid. After this treatment the gas can be tested for methane.

B. Lunge's Modification of the Orsat Apparatus [*].

Fig. 49 shows this apparatus, which, in addition to all the essential parts of an ordinary Orsat apparatus, contains a contrivance for burning hydrogen &c. by means of heated palladium-asbestos. *a* is the gas-burette ; *b*, *c*, and *d* are the usual U-tubes

[*] Added by the Translator.

for absorbing carbon dioxide, oxygen, and carbon monoxide ; k is the ordinary three-way cock ; e is a glass tap, to which is fused a capillary tube bent twice at a right angle. This is tightly joined by a piece of stout india-rubber tubing to the combustion-capillary tube f, which contains a thread of palladium-asbestos, made accord-

Fig. 49.
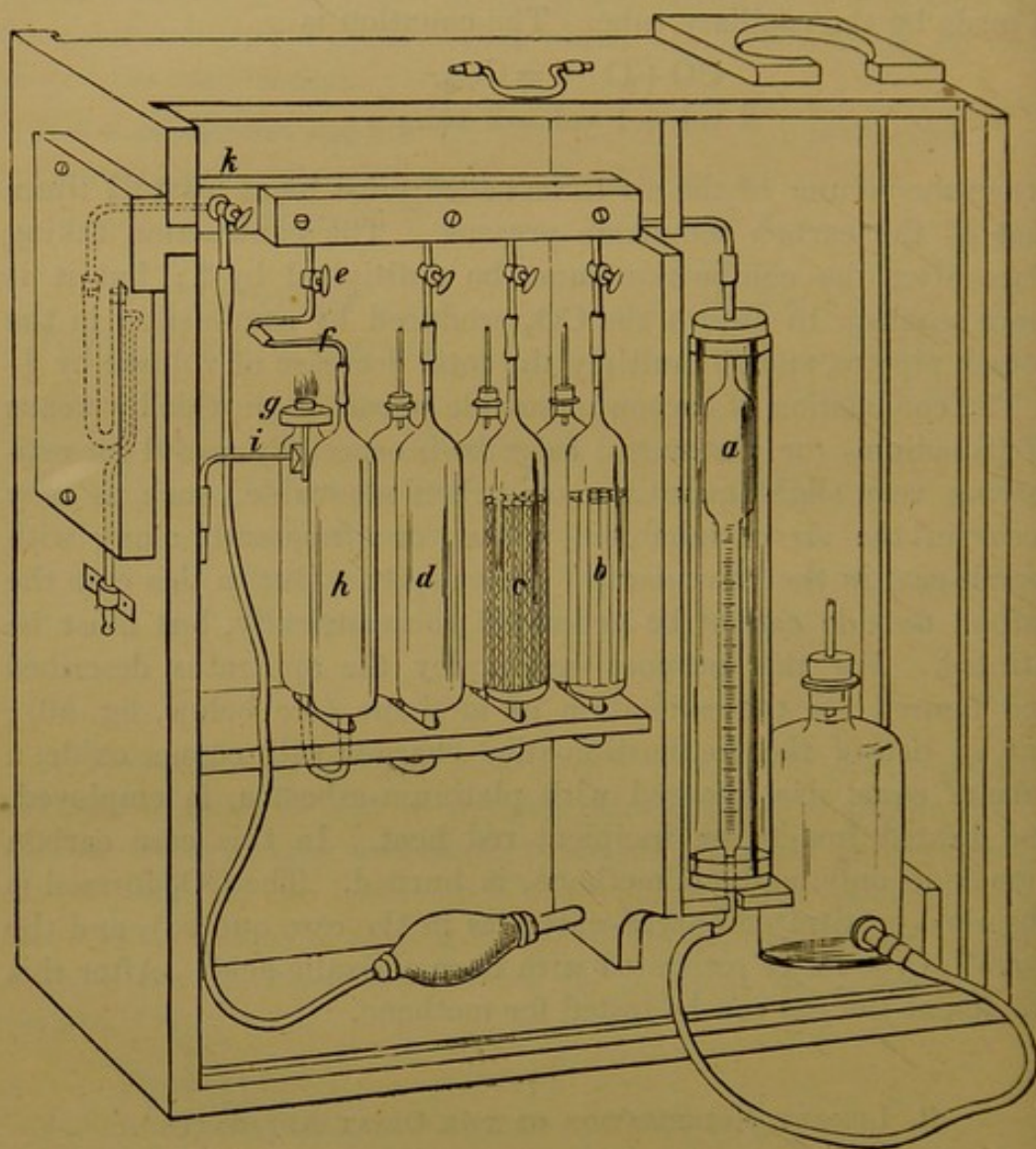
ing to Winkler's description (p. 77). The U-tube h is exactly similar to the vessels b, c, and d, and is filled with water up to a mark in its capillary neck. A very small spirit-lamp, g, is fixed with its thin stem in a spring-clamp which, by means of the pivot-wire i, turns in a socket fastened to the wooden box containing the

apparatus. The dotted U-tube to be seen at the left side is partly filled with cotton-wool, and serves for retaining any tarry matters. (Such a contrivance is generally found connected with the ordinary Orsat apparatus.)

Manipulation.—After absorbing carbon dioxide, oxygen, and carbon monoxide in the manner described p. 49 (any ethylene present would be absorbed along with the carbon monoxide by the acid solution of cuprous chloride), air is admitted through the three-way cock *k* to the gaseous residue contained in the burette *a*, till the total volume as nearly as possible comes up to 100 c. c. The air added will allow of the burning of a quantity of hydrogen corresponding to two fifths of its volume (*i. e.* twice the volume of oxygen contained in the air). This suffices for ordinary producer-gas; but when analyzing "water-gas," or similar mixtures containing a rather considerable quantity of hydrogen, a smaller quantity of gas must be employed for analysis, or else oxygen is introduced in lieu of atmospheric air. After reading off the total volume, the spirit-lamp *g* is lighted and turned so that it heats the capillary *f* very gently; then the level-bottle is raised, the tap *e* is opened, and the gas is passed through the capillary *f* into the receiver *h* and back again into the burette. One end of the palladium-asbestos should become red-hot during this operation. The volume of gas is read off and the passage through *f* is repeated; if, which is usually not the case, a further contraction is now observed, the passage through *f* must be repeated once more. The residual gas is now finally measured, and two thirds of the diminution in volume calculated as hydrogen (compare p. 80).

Application :—

Estimation of hydrogen along with carbon dioxide, oxygen, and carbon monoxide in producer-gas, water-gas, and similar mixtures. The advantage of this apparatus is that it is much more portable than Hempel's burette with its appendages, and that the analysis can be performed in any place and very quickly. Ethylene and other heavy hydrocarbons would be absorbed along 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 they had to be accounted for in another way, a second test should be made, leaving out the operation with cuprous chloride; this time the gas, after absorbing CO_2 and O 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 formed in the receiver b filled with caustic potash, and measuring the new diminution of volume, we obtain another estimation of the combustible gases carbon monoxide, hydrogen, and ethylene (if present) in this way. If the first contraction be diminished by one half of the second contraction (that is, that taking place by absorption of the CO_2 formed in combustion), two thirds of the difference represent the hydrogen ; the carbon monoxide corresponds to the second contraction, according to the following formulæ :—

$$2x \text{ vols. CO} + x \text{ vol. O yield } 2x \text{ vols. } CO_2.$$
$$2y \text{ vols. H} + y \text{ vol. O yield (condensed) } H_2O.$$
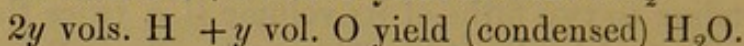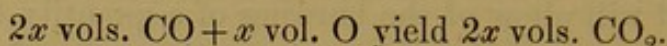
Hence :—

$$\text{First contraction} = A = 3y + x.$$
$$\text{Second contraction} = B = 2x.$$

It follows from this that

$$\text{Carbon monoxide} = B.$$

$$\text{Hydrogen} = 2\frac{\left(A - \dfrac{B}{2}\right)}{3}.$$

If the numbers thus obtained closely agree with those found by the first test, made in the ordinary way, as described before, we may conclude that no heavy hydrocarbons are present ; indeed we must expect to find rather less CO_2 than theory requires, 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 found is in excess of that required on the assumption that only CO and H were present, we must conclude that heavy hydrocarbons were present, and equations might be given including these as well ; but there is no sufficiently accurate method of carrying out this estimation by means of technical gas-analysis, working over water. Ethylene &c. may also be previously absorbed by bromine water (compare p. 59) and estimated in this way.

It is unnecessary to say that any methane present will be left in the unconsumed remainder of gas.

2. *Combustion of Gases with employment of Air and Copper Oxide.*

The apparatus shown in fig. 50, and described in the following passage, serves exclusively for the estimation of methane, by burning the same, absorbing the carbon dioxide formed in titrated baryta-water, and remeasuring the excess of baryta by normal oxalic acid.

The diagram shows the arrangement of an apparatus for examining a sample of pit-air containing fire-damp. The sample of gas is contained in the vessel A; it can be forced from this into the combustion-apparatus by a stream of water from the raised vessel B. The gas first enters the absorbing-worm K, which, in case of need, can also be connected with the gas-holder L, filled with air, or a tube service for compressed air; this worm is filled with concentrated solution of caustic potash (of about 1·26 specific gravity), and serves for retaining every trace of carbon dioxide. From this the gas passes through the drying-bottle S, filled with concentrated sulphuric acid, into the combustion-tube, filled with a layer of granulated copper oxide, 25 centimetres (10 inches) long, and heated to a bright red heat in the furnace V by means of a fourfold burner provided with a contrivance for regulating the supply of gas and air at the same time. The combustion-tube is surrounded by wire gauze for three fourths of its circumference, the gauze being tied fast with wire loops in distances of a few centimetres (about an inch), without pulling the wire loops too tightly; it is then on the outside covered with a thick paste of finely ground fire-clay mixed with a little pipe-clay, so that only the upper fourth, not covered by the wire gauze, remains free. Combustion-tubes thus guarded, when otherwise carefully heated up and cooled down, are very durable and often remain serviceable for months.

From here the gas gets into the absorbing-vessels W and W', and at last into the aspirator N, surmounted by the mercurial pressure-gauge M, whilst the litre-flask O is placed below the outlet-tube in order to measure the water run out.

The apparatus is simplified, if it is to serve for burning smaller volumes of gas, such as in technical gas-analysis form the non-absorbable residue, which cannot be burned by means of palladium-asbestos; this may consist of pure methane or of a mixture

Fig. 50.
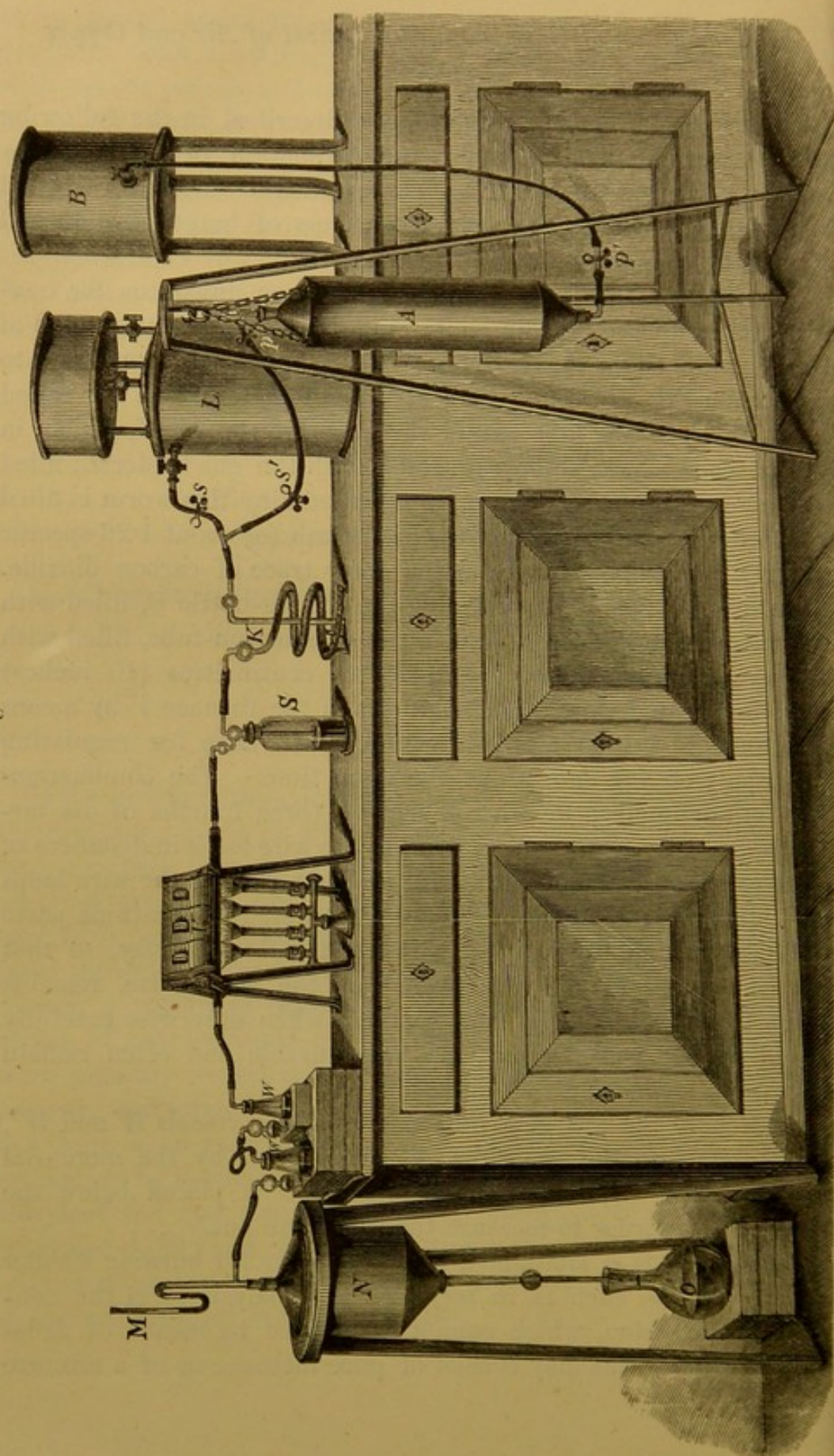
of this with nitrogen. Supposing this residue to have been exactly measured in a Hempel's burette, it is first forced over by a stream of water into a Bunte's burette filled with water; then all the water is run out of this, whereupon the gas is correspondingly diluted with air; the taps are at once shut off, and the burette is fixed in a horizontal position in a stand. Its outlet-tube is now connected by an elastic tube with the absorbing-worm K, the aspirator is started, and with its help, after opening both taps of the burette, the gas is carried through the combustion-apparatus. The air rushing in after serves for sweeping out the burette and the remaining parts of the apparatus.

Manipulation.—Before making a gas combustion, the upper oxide filling of the combustion-tube must be ignited in a current of air or, preferably, of oxygen, until clear baryta-water is no longer affected by the issuing gas, even after passing for some time. With freshly filled tubes this often lasts a remarkably long time; with air especially it may require an ignition of four to six hours' duration. The aim is attained much more quickly by employing a current of oxygen, or by previously igniting the copper oxide in a crucible placed in a slanting position and heated to a full red heat. When the contents of the tube have been sufficiently ignited and all vessels are filled with air free from carbon dioxide, the combustion can begin. The gas-holder L or the air-service must first be shut off by the pinch-cock s, and the pressure-gauge M be made to show an equilibrium.

Suppose we have to examine a sample of air taken from a coal-pit infested with fire-damp, and carried to the laboratory in the well-closed tin-plate cylinder A. First of all the solid corks of this cylinder have to be replaced by simply perforated india-rubber corks, carrying a bent glass tube with a pinchcock-stopper. This change is made by first dipping one end, then the other end, of the cylinder under water, replacing the solid cork by the perforated one below the surface of the water, and then introducing the bent glass tube with its pinchcock-stopper into the perforation of the cork. Since the collecting-vessel had been filled below ground (that is, under higher atmospheric pressure), on opening it a portion of the gas bubbles out through the water, which is the best sign that the stoppings had been tight.

When the tin cylinder A has been arranged in this way it is

hung in its stand, the elastic tube s' is attached to the pinckcock p, and p' is connected with the outlet pipe of the vessel B, after having been filled with water. The pinchcocks p and p' may now be permanently opened, and are for this purpose slid over the adjoining glass tubes. The issue of the gas and the regulation of its current is exclusively performed by the screw pinchcock s'. Before opening the same, the receivers W and W' are charged with 25 c. c. each of approximately normal baryta-water and a drop of phenolphtalein; this quantity is measured off by a burette provided with a float and divided into $\frac{1}{10}$ c. c., and the corks are only opened for an instant. When the receivers are again connected, a little water is run out of the aspirator N, till the baryta-water rises in the bulbs of the receivers; the water run out so far is poured away, and now the current of the gas to be burned is started by gently opening the screw-tap s'. The pressure-gauge M at once begins to rise; the outlet-cock of the aspirator N therefore is opened so far as to show a slight minus pressure, which is maintained throughout the combustion. The current of the gas is so regulated that about 150 bubbles per minute pass through the washing-bottle S, and thus the litre-flask O is filled once in 40 minutes. The water running out is each time poured into the vessel B, closing the aspirator-tap in the meanwhile; the empty flask is at once put in the old place, and each litre-full is noticed.

Once started, the experiment requires but little supervision. The contents of the absorbers now and then are shaken up; in the meantime the state of the barometer and thermometer is noticed, and the baryta-water is standardized by means of normal oxalic-acid solution. Here also a burette with a float is employed. All measurings have to be made very carefully throughout.

After a little time the baryta-water contained in the vessel W becomes turbid, and a distinct precipitate gradually collects in it; but the contents of W' ought to remain clear, or at most slightly opalescent. The volume of gas to be employed for combustion must be adapted to the quantity of the barium carbonate precipitated; 3 or 4 of the 10 litres contained in the cylinder A will be usually consumed, rarely more than 6. In finishing the experiment, the flask O is run full up to its mark for the last time, the tap of the aspirator is closed, and the current of the gas is continued till the pressure-gauge M is in equilibrium. The pinchcock s' is then closed at once, and the volume of gas passed

through the apparatus is now exactly equal to the volume of the water run out.

Now follows the washing-out. The aspirator-tap is once more opened, and air is drawn through the apparatus, by opening the pinchcock s, till the gas remaining in the vessels K and S has been swept out. This may be said to be done with certainty after at most two litres of water are run out ; and the apparatus is now fully in trim for a second combustion. The last operation is to titrate the contents of the receivers W and W' by normal oxalic acid. The diminution of the standard of the baryta-water immediately indicates the volume, expressed in cubic centimetres, of the carbon dioxide formed, and at the same time that of the methane originally present.

The calculation is as follows :—

If $n =$ the volume of methane found,

    $m =$ that of the aspirated gas (*i. e.* the run-out water) in the corrected state,

$n + m =$ the volume of the gas employed for testing,

the amount of methane is $\dfrac{100n}{n+m}$ per cent.

This kind of manipulation includes the measuring of the volume of gas taken, which in this case is rather considerable. But if it is only the question of burning smaller volumes of gas, exactly measured in a burette, the operation is much simpler and shorter. In this case, as already mentioned, the burette is connected with the absorbing-worm K, the aspirator is started, and the gas is slowly sucked through the red-hot copper oxide, the two taps of the burette being opened. The air following upon the gas sweeps out the apparatus ; evidently the water run off does not require to be measured, but this is done approximately, in order to check the operation, and the aspiration is interrupted when 2, or at most 3, litres of water have been run out.

If the gas under examination only consisted of methane and nitrogen, the difference between the volume of the employed gas, measured in the burette, in the corrected state, and that of the methane found by titration, is equal to the volume of the nitrogen.

This method, when carefully carried out, yields very accurate results, and admits of estimating the smallest quantities of methane.

Applications :—

1. *Estimation of methane in fire-damp and in the up-cast currents of coal-pits.*—Operation as just described.

Example :—

Up-cast current of a coal-pit.

Barometer (B), 726 millims.

Temperature (*t*), 23°.

Titre of oxalic acid normal :

$$1 \text{ c. c.} = 1 \text{ c.c. } CO_2 = 1 \text{ c. c. } CH_4.$$

Titre of baryta-water empirical :

$$1 \text{ c. c.} = 0.97 \text{ c. c. normal oxalic acid.}$$

Volume of gas employed = 4 litres.
   or corrected (*m*)   3422·5 c. c.

Baryta-water employed :—

      receiver 1,   25·0 c. c.
         „   2,   25·0 „
                    ————
                    50·0 „   = 48·5 c.c. normal oxalic acid.

Oxalic acid employed for re-titration :—

               receiver 1,   13·9 c. c.
                  „   2,   23·5 „
                            ————
                            37·4 c. c.

               Difference (*n*) = 11·1 c. e.

Found :

$$\frac{100\,n}{n+m} = \frac{100 \times 11\cdot1}{11\cdot1 + 3422\cdot5} = 0.323 \text{ per cent. methane by volume.}$$

2. *Estimation of methane in illuminating-gas, heating-gas, producer-gas, &c.*—Carbon dioxide, ethylene (propylene, butylene), benzene, oxygen, carbon monoxide (comp. p. 59) are first removed and estimated by absorption in turns, the residual gas, or a measured portion of it, being then mixed with a quantity of air, in any case more than sufficient for burning the hydrogen present, and the mixture passed over heated palladium-asbestos in order to estimate the hydrogen (comp. p. 78). From the remaining gas, which, as belonging to the original gas, only contains methane and nitrogen, the oxygen and nitrogen of the air introduced are

deducted; its volume is thus calculated, and it is passed into a Bunte's burette, where it is diluted with a further quantity of air by running out all the water. The contents of the burette are now drawn through red-hot copper oxide in the manner described; the carbon dioxide formed is estimated by titration, and thus we find the methane, and, by difference, the nitrogen.

The constituents occurring in the gas in subordinate quantities, as ammonia, hydrogen sulphide, carbon disulphide, acetylene, are estimated in a larger volume of gas, either by titration (p. 71) or gravimetrically (p. 74).

Example:—

ANALYSIS OF COAL GAS.

Volume of gas employed, 99·1 c. c.

A. *Estimation of the Absorbable Constituents.*

(No correction necessary.)

After absorption by caustic
potash........................... 97·7 c. c.
      Decrease of volume... 1·4 „ = 1·41 volume p. c. of carbon dioxide.

After absorption by bromine
water and removing the bro-
mine vapour by means of
the potash-pipette .... 93·9 „
      Decrease............... 3·8 „ = 3·83 p. c. ethylene, propylene, butylene.

After absorption by fuming
nitric acid and removing the
nitrous vapours by the pot-
ash-pipette...................... 92·9 „
      Decrease............... 1·0 „ = 1·01 p. c. benzene vapour.

After absorption by alkaline
pyrogallol (or phosphorus). 92·6 „
      Decrease............... 0·3 „ = 0·30 p. c. oxygen.

After absorption by cuprous
chloride .... 86·5 „
      Decrease............... 6·1 „ = 6·15 p. c. carbon monoxide.

Non-absorbable remainder ... 86·5 „

B. *Estimation of Hydrogen.*

(No correction required.)

Of the unabsorbed residue of 86·5 c. c., about half is confined in a second burette, as reserve for a check-test; the other portion is mixed with air and burned over heated palladium-asbestos.

Non-absorbable gas employed (corresponding to 46·51 c. c. of the original gas) .... 40·6 c. c.
Gas + air...................................... 99·0 „
Air alone .... 58·4 „
    Containing oxygen .... 12·1 „
        „   nitrogen .... 46·3 „
Volume after combustion................. 65·7 „
Contraction .... 33·3 „
    Corresponding to
Hydrogen (from the gas) .... 22·2 „ = 47·73 p. c. hy-
Oxygen (from the air) .... 11·1 „   drogen.
Not combustible by palladium......... 65·7 „
    Containing
      Oxygen of air (12·1−11·1) = 1·0 „
      Nitrogen of air.............. = 46·3 „
                               ———
              Altogether 47·3 c. c.

Remainder = methane + nitrogen 65·7−47·3 = 18·4 c. c.

C. *Estimation of Methane and Nitrogen.*

(Correction necessary.)

The residue which is not burnt by air over palladium-asbestos, amounting to 65·7, is conveyed into a Bunte's burette, and is then burned by air and copper oxide.

Barometer (B), 736 millims.
Temperature (t), 20° C.
Titre of oxalic acid normal: 1 c. c. = 1 c. c. methane.
    „   baryta water: 1 c. c. = 1·04 normal oxalic acid.
Volume of gas originally employed, 99·1 c. c. = 87·3 corrected.

In 46·51 c. c. of the same (=40·97 c. c. corrected) contained methane + nitrogen 18·4 = 16·2 corrected.

Baryta-water employed 50 c. c. = 52·0 c. c. normal oxalic acid. Oxalic acid employed for reti-

trating .... 37·4 „
_____
Difference...... 14·6 c. c. = 35·63 volume per
cent. methane.

Methane + nitrogen .... = 16·2 c. c.
Methane .... 14·6 „
_____
Difference...... 1·6 c. c. = 3·90 volume per
cent. nitrogen.

Result :—

Carbon dioxide	1·41 volume per cent.	
Ethylene		
Propylene	3·84 „	„
Butylene................		
Benzene vapour.........	1·04 „	„
Oxygen	0·30 „	„
Carbon monoxide	6·15 „	„
Hydrogen	47·73 „	„
Methane..................	35·63 „	„
Nitrogen.................	3·90 „	„
	99·97	

III. Gas-Analysis and Gas-Volumetrical Analysis by means of Lunge's Nitrometer.

(*Added by the Translator.*)

Since the German edition of this book was published, G. Lunge has shown that an instrument, the Nitrometer, constructed by him in 1877 for the analysis of "nitrous vitriol," is capable of an exceedingly large number of uses (some of which had been previously pointed out by A. H. Allen). As one of these uses is that of performing technical gas-analysis, and another that of reducing volumes of gases to normal conditions of temperature and pressure, a diagram and description of the apparatus are appended here.

Fig. 51 shows the construction of Lunge's Nitrometer in the original shape, which is also that best adapted for gas-analysis. *a* is a tube, the "measuring-tube," fitted at the top with a three-way cock, exactly like that belonging to Winkler's or Bunte's gas-burettes (pp. 36 and 42), and a glass cup. The measuring-tube is graduated, the zero-point being the upper end adjoining the tap; from this the graduation is continued downwards up to 50 c. c., each $\frac{1}{10}$ c. c. being marked. The tube is continued about 6 inches below the graduation, and is then tapered off, in order to be joined, by means of a strong india-rubber tube, to a plain cylindrical tube *b*, the "level-tube." Both *a* and *b* are held in strong clamps; that belonging to *a* is preferably a strong spring-clamp, so that the measuring-tube can be taken out and put in in a moment.

Fig. 51.
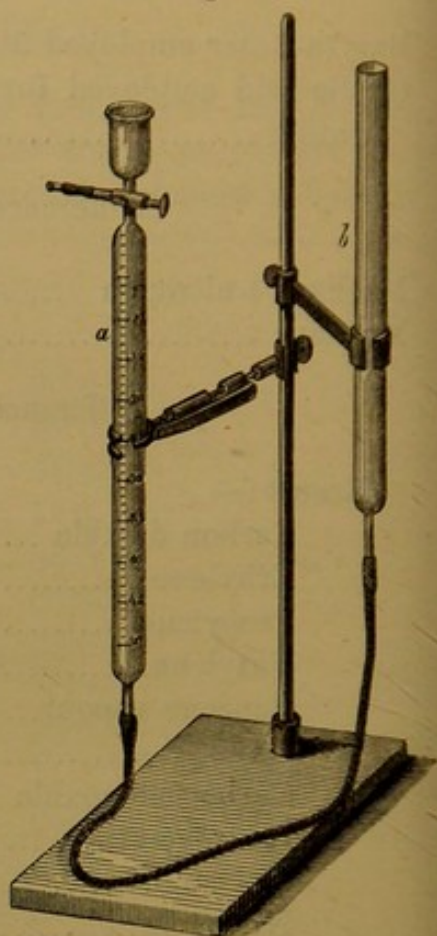
The nitrometer can, of course, be filled with water, or with a solution of a salt, or glycerine, or oil; but the latter substances are always objectionable (comp. p. 27), and Lunge decidedly prefers filling his apparatus with mercury for nearly every use it is put to.

The original use of the nitrometer was *testing the "nitrous vitriol" of sulphuric-acid works* and similar substances by Crum's process, *i. e.* shaking up with strong sulphuric acid and mercury. The same process applies to the analysis of *gaseous mixtures containing the oxides of nitrogen*, which must be first absorbed by strong sulphuric acid, and then submitted to analysis in the nitrometer, where the whole of their nitrogen is liberated in the state of nitric oxide, and can thus be accurately estimated. This process is also very well adapted for the quick and accurate analysis of solid and liquid compounds of nitrous and nitric acid, as the *nitrates and nitrites of soda and potash* (in the case of the

nitrites the whole of the nitrogen is indicated), *pyroxyline, nitro-glycerine, dynamite,* &c. The last-named substances are dissolved in water, or, where this does not act, in sulphuric acid in the cup of the nitrometer itself.

The acid contained in the nitrometer should never be diluted to a greater extent than 2 parts of aqueous liquid to 3 parts of strongest sulphuric acid. The assertion which has been made that strong sulphuric acid *must* be diluted up to this point, or even further, because it keeps nitric oxide in solution, is quite erroneous.

The manipulation of this apparatus is as follows:—It is filled with mercury so far that, on raising the tube *b*, and keeping the tap in the position fig. 52, the mercury stands right in the tap of the tube *a*, and about 2 inches up in the tube *b*. The tap is now closed so that its ways communicate neither with the inside nor the outside of the tube *a*, and a certain volume of nitrous vitriol (from 0·5 to 5 c. c., according to strength) is poured into the cup; the tube *b* is lowered, and the tap cautiously opened so as to assume the position fig. 52, and shut briskly when all the acid has run out except a small drop, but no air has as yet entered. The cup is now rinsed by pouring about 3 c. c. of strong pure sulphuric acid into it; this is drawn into the tube *a*, and this rinsing repeated with another 2 or 3 c. c. of pure acid, always avoiding the entrance of the smallest bubble of air into the tube *a*. The tube *a* is now taken out of the clamp and the evolution of gas started by inclining it several times almost to the horizontal, and suddenly righting it again, so that the mercury and the acid are well mixed and shaken for one or two minutes till no

Fig. 52.
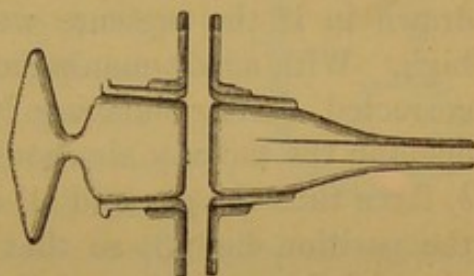
Fig. 53.
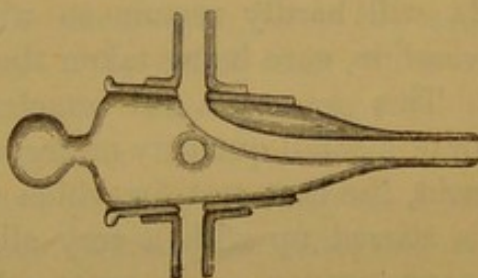
Fig. 5
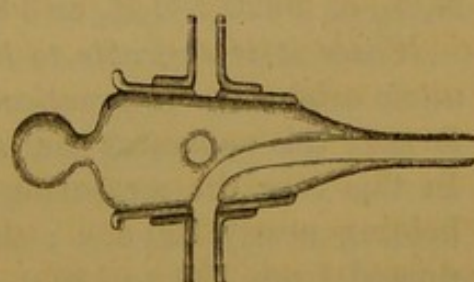
more gas is given off. Tubes are so placed that the mercury in *b* is as much higher than that in *a* as is required for balancing the acid in *a*; this will take 1 millim. of mercury for $6\frac{1}{2}$ millims. of acid. After the gas has assumed the temperature of the room and all froth has subsided, which will take about 10 to 15 minutes, the volume of the gas is read off, and also that of a thermometer hung up close by, and a barometer, or else the volume of air in the reducing-apparatus (fig. 19, p. 24) or that to be described below. In order to check the level, open the tap, when the level of the mercury in *a* should not change. If the mercury rises, too much pressure has been given, and the reading must be increased a little, say 0·1 c. c. If it sinks, the opposite must take place, that is always in the opposite sense to the change of level. Another plan is, to put a little acid into the cup before opening the tap. This would be drawn in if the pressure were too low, or raised if it were too high. With adroit manipulation the experiment can then soon be corrected. After finishing it, lower the graduated tube *a*, lest on opening the tap any air should enter; open the tap, raise the tube *b*, force thus the gas and all acid into the cup, and put the tap in the position fig. 53, so that the acid flows out and into a vessel placed below; the last of it is drawn out by blotting-paper. The nitrometer is then ready for the next experiment. A test must always be made to ascertain whether the glass tap is gas-tight. It will hardly remain so without greasing it occasionally with vaseline, care being taken that no grease gets into the bore.

This process is not interfered with by the presence of chlorides or of a small quantity of organic substance, but it is by sulphurous acid, the best test for which is the smell. To remove it, the acid is stirred up with a very slight quantity of powdered potassium permanganate; any great excess of this makes the process very troublesome and inaccurate. Each c. c. of gas, reduced to 0° and 760 millims., is equal to 0·627 mg. N, or 1·343 mg. NO, or 1·701 N_2O_3, or 2·820 NO_3H, or 3·805 mg. $NaNO_3$.

Where it is desirable to liberate and measure a larger volume of nitric oxide than is practicable in the ordinary nitrometer, another form of this apparatus can be employed. This is shown in fig. 55. In this case the measuring-tube is provided with a strong bulb, holding nearly 100 c. c.; the cylindrical part below this is graduated from 100 to 140 c. c. The level-tube is provided with a similar bulb at the bottom, to receive the mercury forced out of

the measuring-tube; it may also be provided with a graduation similar to that of the latter, for the purpose of facilitating the level of the liquids.

Fig. 55.

The manipulation with nitrate of soda or similar substances, containing a large proportion of nitrogen acids, is as follows:—Such a quantity of substance is taken that it will in any case give off more than 100 c. c., but less than 140 c. c., of nitric oxide at the existing temperature and pressure. In the case of commercial nitrate of soda, for instance, it will amount to about 0·35 grammes. This is facilitated by employing a narrow weighing-tube with a mark indicating 0·35 grammes. Put the sample, finely ground if solid, into the tube up to the mark, cork the tube, weigh it, pour the contents into the cup of the nitrometer, taking care that the substance gets as much as possible upon the bottom of the cup, and re-weigh the small tube.

The three-way cock must have been made to communicate neither above, nor below, nor sideways. In the case of solid nitre and the like, about 0·5 c. c. water is run in, and when the nitre is nearly or quite dissolved, the solution is drawn into the measuring-tube by cautiously opening the tap, the levelling-tube being lowered, the cup is washed with, at most, 0·5 c. c. water, and 15 c. c. concentrated pure sulphuric acid run in. The operation is in other respects performed as described above.

The nitrometer should first be tested whether it really contains exactly 100 c. c. at the mark 100, for instance, by inverting it, filling in mercury to the mark 100, running it off, and weighing. It should weigh 1396 grammes, reduced to 0°. If there is a difference, this must be allowed for in every reading.

This form of nitrometer is also very well adapted as an *apparatus for reducing the volume of gases to the normal state without observing the thermometer and barometer*, more convenient than that shown in fig. 19, p. 24. For this purpose the three-way tap may be replaced by a simple tap, the cup and the bulb of the level-tube can be dispensed with; but none of these pieces, if present, interfere with the working of the apparatus. First of all, it is calculated what volume 100 c. c. of air, taken in the normal state, would
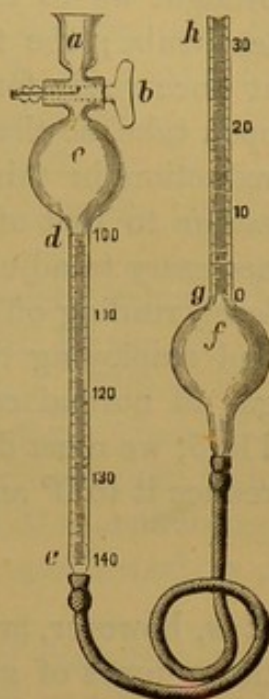
occupy at the temperature and pressure existing at the time of
preparing the apparatus; the mercury in the measuring-tube is
brought up to this point by opening the tap and adjusting the
level-tube; the tap is now closed, and the apparatus is evidently
at once ready for acting at any time by raising or lowering the
open tube, so that the mercury in both tubes is at a level. The
reduction in this case would apply to gases in the dry state, or
rather to that of the air enclosed. For this purpose it is only
necessary to adjust the tubes so that the liquids are exactly at a
level, reading off the volume confined within the measuring-tube,
and employing this as a factor for reducing any other volume of
gas to normal conditions. Suppose the reading of the day was
110·5, we must divide every other reading n by 1·105, in order to
reduce it to 0° and 760 millims.; for

$$110\text{·}5 : 100 :: n : x.$$

It is, however, preferable to adjust the apparatus so that it reduces
the volumes of gases to 0° and 760 millims. when taken in a state
of saturation with moisture. For this purpose we put about 1 c. c.
of water into the measuring-tube, and an equal height of water
into the level-tube; we shall then obtain the air saturated with
moisture, and can calculate its volume by the formula given on p. 25.
We may then employ the apparatus equally well for reducing dry
gases to the normal state, by adjusting the tubes so that the
mercury in the outer tube stands higher than that in the inner
tube by as many millimetres as correspond to the tension of
aqueous vapour at the existing temperature (Table 6).

As an apparatus for gas-analysis proper it is, in most cases, best
to employ the nitrometer (fig. 51). It is quite evident that it will
fulfil all the functions of Hempel's gas-burette (p. 52), by attach-
ing to the side-opening of the three-way cock the various pipettes
described, pp. 54 & 55, or similar pipettes on a smaller scale,
partially filled with mercury, as described by Lunge (*Berichte der
deutschen chemischen Gesellschaft*, vol. xiv. pp. 21, 92) and by
Hempel in more recent publications. The applications possible
in this way are described on pp. 58 & 59. The nitrometer enjoys
a great advantage over Hempel's burette in being filled with mer-
cury, by admitting of more accurate readings of level, and by being
adapted to the examination of gases partially soluble in water,
whence it also completely replaces the "modified Winkler's gas-

burette" (fig. 40). In some cases it may serve, like Bunte's gas-burette (p. 42), without any absorption-pipettes, but far more conveniently than Bunte's burette, namely, by introducing the reagents through the cup and the three-way cock; but this can only be done, either if only one of the constituents has to be estimated (for instance, carbon dioxide), or where the reagent required for estimating a second constituent does not interfere with the first, as when we first estimate carbon dioxide by means of caustic potash, and subsequently oxygen by pyrogallol.

In every case the gas to be tested is first passed through the tubes and out of the cup in the position fig. 53, till all the air has been driven out and pure gas issues from the tap. This is then put into the position fig. 54, a suitable quantity of gas (preferably 50 c. c.) is drawn into the measuring-tube by lowering the level-tube, the tap is put back in the position fig. 53, the conducting-tube is detached from it, and the analysis is performed as is explained above.

The nitrometer can be very well employed for *collecting, measuring, and analyzing the gases dissolved in water or other liquids*, by attaching to the side-tube of the three-way cock a flask filled with the liquid to be tested. This is connected with the cock by an india-rubber stopper, a short elbow-tube, and a short stout piece of india-rubber tubing. The flask is filled very nearly to the top; when the stopper is pressed down the liquid will enter into the tubing and fill all the space up to the tap, which is first put like fig. 53, then like fig. 54. The liquid is now heated till the gas is expelled, and this is collected in the measuring-tube, the level-tube being lowered as much as possible, thus facilitating the expulsion of the gases by aspiration. When all the gas has been expelled, the tap is put as in fig. 53; the gas, after cooling, is measured, and is analyzed by submitting it to various absorbents, as described above.

The nitrometer is also a very convenient apparatus *for the volumetrical analysis of a great many substances*, namely, for all cases of analytical operations in which *a definite quantity of a gas is liberated which is not soluble to a very considerable extent in the liquid from which it is liberated, and which does not act upon mercury*. Sometimes the operation can be carried on within the measuring-tube itself, and this is even preferable when only small quantities of gas have to be estimated. In this case the nitrometer

is treated as described for the analysis of nitrate of soda and
similar substances, only it is not possible, of course, to use the
form of apparatus shown in fig. 55, but that shown in fig. 51
(p. 96). The measuring-tube is filled with mercury up to the tap,
the latter is closed, the level-tube is lowered, the substance to be
tested is introduced exactly like the nitrate of soda, without allow-
ing any air to enter, the decomposing reagent is then introduced
in a similar way, and the operation is finished by agitating the
tube, levelling the mercury, and reading-off the volume of gas.

In a few cases the nitrometer should not be filled with mercury,
but with a solution of salt, as recommended by Mr. A. H. Allen;
but this is only required very rarely, for instance in testing sweet
spirit of nitre, by adding a solution of potassium iodide and sul-
phuric acid, and measuring the nitric oxide liberated. In this case
the mercury would be acted upon, and hence cannot be employed;
but in nearly every other case mercury is very much to be pre-
ferred to solutions of salt or sulphate of soda &c., as mentioned on
p. 27.

This is decidedly the case when employing a *decomposition flask*
provided with an inner tube fused on to its bottom, or (less con-
veniently, because it is more liable to breakage) simply placed
inside the flask so as to lean against its side in an upright position.
The flask is attached to the lateral opening of the nitrometer tap
exactly as that described above, which serves for estimating the gases
dissolved in water. This arrangement is the most convenient one
for most purposes; the reaction then takes place outside the
nitrometer, and the latter only serves for measuring the gas
liberated, not directly, as in most cases the bulk of the gas will
remain within the decomposition flask, but by the displacement of
an equal volume of air from the flask, tubes, &c. In this case it
is not necessary, or even advisable, to fill the nitrometer imme-
diately up to the tap, that is to the zero point; it is preferable to
start with 1·0 c. c., or any other point below the tap, which obviates
the danger of any mercury running over into the decomposition
flask when carelessly opening the tap. It is hardly necessary to
say that the volume of air left in the nitrometer before the
operation, must be exactly read off and deducted from the final
reading. Special nitrometers are now made for this purpose, with
a tap possessing only the curved axial bore, and not surmounted by

a cup; the division begins a short distance below the tap, which facilitates the reading.

The action of the decomposition flask will be best understood by describing a special case. We shall select for this

A. *The analysis of ammonia salts, or of urine*, by means of Knop's brominated soda. This reagent is prepared by dissolving 100 grammes of good commercial caustic soda (70 per cent.) in 250 c. c. of water, and cautiously adding 25 grammes of bromine. It must be kept in a dark cool place, but even then does not keep unchanged for any considerable time, and hence it should be prepared fresh every few days. As this is rather an irksome operation, owing to the deleterious fumes and the extremely corrosive action of bromine, it is best to employ Dr. Frank's "bromum solidificatum"—that is, sticks of hardened kieselguhr, impregnated with bromine, and containing a definite quantity of that agent for a certain length of stick, for example 1 gramme for 1 centimetre in length. In this case a solution of 400 grammes caustic soda in a litre of water is kept in stock, and every few days a sufficient quantity is converted into Knop's reagent simply by adding to each 100 c. c. a quantity of bromine-sticks representing 10 grammes of bromine. The bromine dissolves in the caustic liquor by agitating; the sticks remain in the liquid without causing any trouble.

This reagent liberates the nitrogen contained in ammonia salts, also that of urea, uric acid, and many other organic compounds. The reaction is not altogether complete, but it is sufficiently constant to base upon it very exact estimations of ammonia salts, and very approximate ones of urea, the latter in any case superior to any other known method of testing urine. If the flask is thoroughly shaken after the liquids have been mixed and allowed to cool down to the temperature of the room, the gas liberated indicates 97·5 per cent. of the ammonia, or 91 per cent. of the urea present. Hence we must increase each reading by 2½ per cent. of its amount in the former, or by 9 per cent. in the latter case. Especially in the case of ammonia the results will be within 0·5 per cent. of the real percentage, or even nearer.

The operation is carried on in this manner. The ammonia salt, preferably dissolved in water, or the urine &c., is introduced into the outer space of the decomposing flask. This is best done by means of an accurate pipette, graduated into hundredths of a

c. c.   About 25 or 30 c. c. of the brominated soda is then poured
into the inner tube.   Meanwhile the cork must have been attached
to the nitrometer-tap by means of a short stout elastic tube, which
will allow the flask to hang on the nitrometer without any special
support.   The tap should be turned as in fig. 53.   The cork is
now pressed tightly down into the flask, the tap turned as in fig.
54, the flask inclined so that the contents of the tube mix with
the liquid outside, and shaken till no more gas is given off, which
takes about a minute.   The mercury-levels are roughly adjusted,
the apparatus allowed to stand for $\frac{1}{4}$ hour in order to cool down
(whether this is complete will be seen by the level remaining
stationary), the levels adjusted exactly, and read off.   The volume
of gas, taken as saturated with moisture, is reduced to $0°$ and
760 millims., either by reading the thermometer and barometer and
employing the Table 6 (p. 115), or by means of the apparatus fig. 55,
in the way described p. 99.   Each c. c. of gas indicates $0·001254$
gramme N, or nominally $0·001523$ gramme NH_3, or $0·002687$
gramme CON_2H_4; but, according to what has been said above,
it really indicates $0·001562$ gramme NH_3, or $0·002952$ gramme
CON_2H_4.   Since, however, the uric acid &c. contained in urine
is also decomposed, it is near enough the truth for medical
purposes to assume the first-given figure for urea, namely
$0·002687$.

B. Precisely the same course is followed when liberating *carbon
dioxide*.   In this case the carbonate is best placed outside, the acid
within the inner tube.   This process can be utilized :—

1. For the analysis of *commercial soda or potash*, in the following
    manner.   When employing the sample as it is, merely the
    carbonate contained in it is estimated.   But by first evapo-
    rating the sample with ammonium carbonate and igniting, the
    caustic alkali is also converted into carbonate, so that in this
    test the total available alkali is estimated (except as to silicate
    and aluminate).
2. For the analysis of *bicarbonates*, both as solids or dissolved in
    water.   This is specially useful when combining it with the
    ordinary alkalimetrical testing.
3. For the estimation of the *carbonate contained in commercial
    caustic soda*, or in the *solutions obtained in causticizing soda-
    ash*, or in *soap-maker's leys*.

4. For the estimation of *calcium carbonate* in *limestone, marl, quick-lime, bone-charcoal* of sugar-works, &c.

5. For *estimating acids* by adding to them an excess of sodium or calcium carbonate. This is especially useful for *acetic acid*; but it is also serviceable for mineral acids in cases in which no delicate balance, weights, and standard liquors are at hand.

6. For estimating the *free acid* contained in many metallic salts, as zinc chloride, manganous chloride, cupric sulphate, &c.

7. For estimating *manganese ore, Weldon mud*, &c. by means of oxalic acid.

8. For estimating *oxalic acid* or *oxalates* by means of MnO_2.
   And for other purposes.

It cannot be expected that completely exact results will be obtained in this case, since carbon dioxide is very sensibly soluble in the decomposing liquid; nor can this circumstance be taken into account in such a simple way as in the preceding case, since the solubility of CO_2 depends upon its tension, and this greatly varies, even for vessels of the same capacity, with the amount of CO_2 given off and mixed with the air originally present. It is not of any use to facilitate the liberation of the carbon dioxide by aspiration, or by heating; as in any case the equilibrium of pressure and temperature must be restored, whereby any CO_2 previously liberated will act upon the liquid as before. The following table (by E. Dietrich) shows what is the proportion to be added for varying quantities of CO_2 given off, if always the same quantity of acid is employed, namely 5 c. c. of spec. grav. 1·125. Even with the use of this table this mode of testing, unless the operator has previously checked it for his own apparatus, cannot be recommended for very exact estimations, but merely for rapid technical tests, requiring no balance and weights, and easily performed even by unskilled experimenters. The results obtained with it, if properly performed, are within 0·5 per cent. of the truth.

Table showing the Absorption of Carbon Dioxide by 5 c. c.
hydrochloric acid of spec. grav. 1·125.

Given off, c. c....	1	2	4	6	8	10	12	14	16	18	20	22	24
Absorbed, c. c....	1·85	2·00	2·31	2·62	2·93	3·24	3·55	3·86	4·17	4·48	4·79	4·96	4·98
Given off, c. c....	26	28	30	32	34	36	38	40	42	44	46	48	50
Absorbed, c. c....	5·03	5·06	5·09	5·11	5·14	5·17	5·20	5·23	5·25	5·27	5·30	5·32	5·35
Given off, c. c....	55	60	65	70	75	80	85	90	95	100			
Absorbed, c. c....	5·41	5·48	5·55	5·62	5·69	5·76	5·83	5·90	5·97	6·04			

The figures found in the second line should be added to those
read off in the first line, *before* reducing the volume to 0° and
760 millim.

C. Very accurate and convenient analytical estimations can be
performed by means of *hydrogen peroxide*. This substance, when
brought into contact with other compounds containing oxygen in
the "active" state, reacts with them in such a way that the
active oxygen of *both* substances is given up, and liberated as
inactive oxygen gas, but in exactly equal proportions, so that
half of it always belongs to the substance of which there was no
excess present, and which can be thus estimated; the other half
issuing from the other substance present in excess, that excess
being unaffected in the reaction. Thus

(1) *Hydrogen peroxide* itself can be most accurately estimated
by its reaction with an acidified solution of potassium per-
manganate, by operating in this way. A certain quantity, say
2 c. c., of the hydrogen peroxide is put into the decomposition
flask, and an excess of potassium permanganate, with some sulphuric
acid, into the inner tube. The flask is attached to the nitrometer,
and the operation started as described on p. 103. It is seen, by the
colour of the liquid, whether there was an excess of permanganate
present, as is necessary in this case. The decomposition takes
place almost instantaneously, and all the oxygen is given off by a
little shaking, no sensible quantity of it remaining dissolved in
the liquid. By dividing the oxygen liberated by 2, we obtain
that belonging to the hydrogen peroxide. The reaction is

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10O.$$
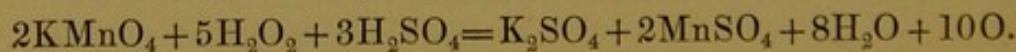
Each c. c. of oxygen, reduced to 0° and 760 millim. (allowing it to exist in the moist state), is equal to 0·001433 gramme of active oxygen.

(2) *Potassium permanganate* is tested precisely in the same way, but by employing an excess of hydrogen peroxide. In this case it is preferable to put the latter in the inside tube, the former in the outer space, adding an excess of dilute sulphuric acid. After the reaction the liquid ought to be colourless, showing that all the permanganate has been decomposed. This process admits of *exactly* standardizing solutions of potassium permanganate without balance and weights, and without knowing the percentage or even the volume of the H_2O_2 employed.

(3) *Manganese ore, Weldon mud*, &c., are tested exactly in the same way, after adding an excess of dilute sulphuric acid and driving off any carbonic acid present. Only then the flask is attached to the nitrometer, and the hydrogen peroxide is mixed with the substance by tilting the flask.

(4) *Bleaching-powder* (chloride of lime), *bleach-liquor*, &c. are also exactly tested by hydrogen peroxide in the same way. Each c. c. of oxygen (that is, half of that liberated) is =0·006341 gramme of available chlorine. Hydrogen peroxide may conversely be tested by an excess of bleaching-liquor, exactly as by potassium permanganate.

(5) *Potassium ferricyanide*, if an excess of sodium hydrate is present, behaves exactly like the foregoing substances, and is thereby completely reduced to ferrocyanide.

D. *Nitrous vitriol, nitrate of soda*, &c., can be tested by shaking them up in the decomposition flask with an excess of strong sulphuric acid and mercury, after having replaced the air by hydrogen or carbon dioxide.

E. The above cases are given as examples; but it is evident that a number of other analytical operations of similar order can be performed by means of the nitrometer. But this instrument lends itself also to another class of analyses, namely, that *where a substance is tested by its absorbing action upon gases*. We may mention, as an instance of this, the *testing of indigo*, for which, as is well known, we do not possess very accurate methods. A solution of reduced indigo is prepared, by digesting a weighed

quantity with an excess of caustic soda, grape-sugar, and alcohol (Fritsche's vat). The nitrometer is filled with air down to the lowest point of the graduation, and the cup filled with carbon dioxide, to prevent premature oxidation of the sample; a measured quantity of the reducing solution is introduced into the cup, then into the measuring-tube, and is shaken up with air. The reduction of volume produced is a measure of the oxygen taken up for oxidizing the indigotine. Each c. c. of oxygen, reduced to $0°$ and 760 millim., is equal to $0 \cdot 02347$ gramme indigotine ($C_{16}H_{10}N_2O_2$). If we dissolve $46 \cdot 94$ grammes of indigo in a litre, and employ 5 c. c. for each test, each $0 \cdot 1$ c. c. is $= 1$ per cent. indigotine; or if we employ 10 c. c., each $0 \cdot 2$ c. c. $= 1$ per cent. indigotine. In this case also the operation can be performed by introducing the reduced indigo solution into the decomposition flask; larger quantities can thus be operated upon.

APPENDIX.

1. *Atomic Weights.*

Element.	Symbol.	Atomic weight.	Element.	Symbol.	Atomic weight.
Aluminium	Al	27·01	Lead	Pb	206·47
Antimony	Sb	119·96	Magnesium	Mg	23·96
Arsenic	As	74·92	Manganese	Mn	53·91
Barium	Ba	136·76	Mercury	Hg	199·71
Bismuth	Bi	207·52	Nickel	Ni	57·96
Boron	B	10·95	Nitrogen	N	14·02
Bromine	Br	79·77	Oxygen	O	15·96
Calcium	Ca	39·99	Palladium	Pd	105·74
Carbon	C	11·97	Phosphorus	P	30·96
Chlorine	Cl	35·37	Platinum	Pt	194·41
Chromium	Cr	52·01	Potassium	K	39·02
Cobalt	Co	58·89	Silver	Ag	107·67
Copper	Cu	63·19	Silicium	Si	28·20
Fluorine	F	18·98	Sodium	Na	22·99
Gold	Au	196·19	Strontium	Sr	87·37
Hydrogen	H	1·00	Sulphur	S	31·98
Iodine	I	126·56	Tin	Sn	117·70
Iron	Fe	55·91	Zinc	Zn	64·90

2. *Calculated Densities and Litre-weights of Gases and Vapours.*

Name of the gas.	Molecular formula.	Density.	1 litre of the gas in the normal state weighs
			grammes
Acetylene	C_2H_2	12·970	1·1621
Air (atmospheric)*	......	14·422	1·2922
Ammonia	H_3N	8·510	0·7625
Antimoniuretted hydrogen	H_3Sb	62·545	5·6040
Arseniuretted hydrogen	H_3As	38·960	3·4908
Benzene...........................	C_6H_6	38·910	3·4863
Butylene	C_4H_8	27·940	2·5034
Carbon monoxide.......................	CO	13·965	1·2512
Carbon dioxide........................	CO_2	21·945	1·9663
Carbon disulphide	CS_2	37·965	3·4017
Carbon oxysulphide	COS	29·955	2·6839
Chlorine............................	Cl_2	35·370	3·1691
Cyanogen	$(CN)_2$	25·990	2·3287
Ethane	C_2H_6	14·970	1·2413
Ethylene	C_2H_4	13·970	1·2517
Hydrogen	H_2	1·000	0·0896
Hydrogen chloride	HCl	18·185	1·6293
Hydrogen cyanide	$HCN·$	13·495	1·2091
Hydrogen sulphide	H_2S	16·990	1·5223
Methane	CH_4	7·985	0·7154
Nitrogen	N_2	14·020	1·2562
Nitrogen protoxide	N_2O	22·000	1·9712
Nitric oxide	NO	14·990	1·3431
Nitrogen trioxide.....................	N_2O_3	37·960	3·4012
Nitrogen peroxide†	NO_2	22·970	2·0581
Oxygen	O_2	15·960	1·4300
Phosphoretted hydrogen	H_3P	16·980	1·5214
Propylene	C_3H_6	20·955	1·8775
Silicium tetrafluoride	SiF_4	52·055	4·6641
Sulphur dioxide	SO_2	31·950	2·8627
Water	H_2O	8·980	0·8046

* The calculation of the specific and litre weight of atmospheric air has been made on the basis of the average percentage of oxygen$=20·745$ per cent. by volume, as found by P. v. Jolly.

† This compound, as actually existing at temperatures not too much above the ordinary temperature, is a mixture of molecules of N_2O_4 and NO_2. The calculation has been made on the basis of the formula NO_2.

3. *Changes of Volume when Gases are burnt in Oxygen.*

Name of gas.	Molecular formula.	Combustion requires combustible gas. vols.	oxygen. vols.	Combustion yields aqueous vapour (condensed). vols.	carbon dioxide. vols.	Volume of gas before combustion. vols.	after combustion. vols.	after combustion and absorption of carbon dioxide. vols.	Contraction after combustion. vols.	ratio of combustible gas to contraction.	after combustion and absorption of CO₂. vols.	ratio of combustible gas and absorption combustible gas to contraction.
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	$\frac{2}{17}$
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	0	4	$\frac{1}{2}$	6	$\frac{1}{3}$
Propylene	C_3H_6	2	9	6	6	11	6	0	5	$\frac{2}{5}$	11	$\frac{2}{11}$

4. *Heat of Combustion of Solid, Liquid, and Gaseous Bodies,*

for 1 kilogramme of substance, expressed in calories, one of which = the heating of 1 kilogramme water from 0° to 1° C.

1 kilog. substance.	Burning to	Gives off calories.	Observer.
Acetylene, C_2H_2	$2CO_2+H_2O$ (liquid)	11,945·0	Thomsen.
,,	$2CO_2+H_2O$ (steam)	11,529·6	,,
Arsenic	As_2O_3	1,030·5	,,
Benzene, C_6H_6	$6CO_2+3H_2O$ (liquid)	10,330.7	,,
,,	$6CO_2+3H_2O$ (steam)	9,915·3	,,
Bismuth	Bi_2O_3	95·5	Woods.
Carbon: wood-charcoal	CO	2,473·0	Favre and Silbermann.
,, ,,	CO_2	8,080·0	,, ,,
,, sugar-coal	,,	8,039·8	,, ,,
,, gas-retort coal	,,	8,047·3	,, ,,
,, blast-furnace graphite	,,	7,762·3	,, ,,
,, natural graphite	,,	7,796·6	,, ,,
,, diamond	,,	7,770·1	,, ,,
Carbon monoxide, CO	,,	2,441·7	Thomsen.
Carbon disulphide, CS_2	$2SO_2+CO_2$	3,400·0	Favre and Silbermann.
Copper	Cu_2O	321·3	Thomsen.
,,	CuO	593·6	Joule.
Ethane, C_2H_6	$2CO_2+3H_2O$ (liquid)	12,444·4	Thomsen.
,,	$2CO_2+3H_2O$ (steam)	11,364·3	,,
Ethylene, C_2H_4	$2CO_2+2H_2O$ (liquid)	11,957·1	,,
,,	$2CO_2+2H_2O$ (steam)	11,185·9	,,
Hydrogen	H_2O (liquid)	34,180·0	,,
,,	H_2O (steam)	28,780·0	,,
Iron	FeO	1,352·6	Favre and Silbermann.
,,	Fe_3O_4	1,582·0	,, ,,
,,	Fe_2O_3	2,028·0	,, ,,
Lead	PbO	243·0	Thomsen.
Magnesium	MgO	6,077·5	,,
Manganese	MnO	1,724·0	,,
,,	MnO_2	2,113·0	,,
Mercury	Hg_2O	105·5	,,
,,	HgO	153·3	,,
Methane, CH_4	CO_2+2H_2O (liquid)	13,345·6	,,
,,	CO_2+2H_2O (steam)	11·995·6	,,
Nitrogen	N_2O	— 654·3	,,
,,	NO	−1,541·1	,,
,,	NO_2	— 143·2	,,
Nitrogen monoxide, N_2O	NO	— 564·3	,,

Table (*continued*).

1 kilog. substance.	Burning to	Gives off calories.	Observer.
Nitric oxide, NO	NO_2	652·3	Thomsen.
Phosphorus	P_2O_5	5,964·5	,,
Potassium	K_2O	1,745·0	Woods.
Propane	$3CO_2+4H_2O$ (liquid)	12,125·0	Thomsen.
,, ...	$3CO_2+4H_2O$ (steam)	11,136·3	,,
Propylene, C_3H_6	$3CO_2+3H_2O$ (liquid)	11,790·4	,,
,, ...	$3CO_2+3H_2O$ (steam)	11,019·0	,,
Silicium	SiO_2	7,830·0	,,
Silver	Ag_2O	27·3	,,
Sulphur, rhombic	SO_2	2,221·3	,,
,, monoclinic...............	....	2,241·4	,,
Sulphuretted hydrogen	SO_2+H_2O (liquid)	2,741·0	Favre and Silbermann.
,, ,, ...	SO_2+H_2O (steam)	2,457·0	,, ,,
Tin.................................	SnO	573·6	Andrews.
,, ...	SnO_2	1,147·0	,,
Zinc	ZnO	1,314·3	Thomsen.

5. *Standard Solutions for Technical Gas-analyses.*

1 vol. gas at 760 millims. and 0°, dry.	Formula.	Indicated by 1 vol. normal solution, containing per litre	
Ammonia	NH_3	grammes 2·1911 Sulphuric acid	SO_4H_2
,, ...	,,	2·5078 Potassium hydroxide...	KOH
Carbon monoxide ...	CO	4·0222 Oxalic acid, sublimed...	$C_2H_2O_4$
,, ,,	,,	5·6314 ,, ,, crystallized	$C_2H_2O_4, 2H_2O$
,, ,,	,,	7·6468 Barium hydroxide	$Ba(OH)_2$
,, ,,	,,	14·0835 ,, ,, cryst.	$Ba(OH)_2, 8H_2O$
Carbon dioxide	CO_2	4·0222 Oxalic acid, sublimed...	$C_2H_2O_4$
,, ,, ...	,,	5·6314 ,, ,, crystallized	$C_2H_2O_4, 2H_2O$
,, ,, ...	,,	7·6468 Barium hydroxide	$Ba(OH)_2$
,, ,, ...	,,	14·0835 ,, ,, cryst.	$Ba(OH)_2, 8H_2O$
Chlorine...............	Cl	4·4288 Arseniousacid,dissolved in sodium bicarbonate.....................	As_2O_3
,, ...	,,	11·3396 Iodine, dissolved in potassium iodide	I

TABLE (*continued*).

1 vol. gas at 760 millims. and 0°, dry.	Formula.	Indicated by 1 vol. normal solution containing per litre.	
		grammes	
Hydrogen chloride...	HCl	4·8233 Silver, dissolved in nitric acid	Ag
„ „ ...	„	3·4042 Ammonium sulphocyanide	CNS, NH₄
„ „ ...	„	2·5078 Potassium hydroxide ...	KOH
Methane	CH₄	4·0222 Oxalic acid, sublimed...	C₂H₂O₄
„	„	5·6314 „ „ crystallized	C₂H₂O₄, 2H₂O
„	„	7·6468 Barium hydroxide	Ba(OH)₂
„	„	14·0835 „ „ cryst.	Ba(OH)₂, 8H₂O
Nitrogen trioxide ...	N₂O₃	5·6186 Potassium permanganate	KMnO₄
Sulphur dioxide ...	SO₂	11·3396 Iodine in Potassium iodide	I

6. *Table for Reducing Volumes of Gases to the Normal State.* By Professor Dr. LEO LIEBERMANN.

[Communicated by permission of the Author.]

Instructions for Use.

Suppose the volume of a gas to have been found = 26·2 c. c. at 742 mm. barometric pressure, 18° C. temperature, saturated with moisture. In order to reduce it to the normal state (760 mm., 0° C., dry), we proceed as follows :—

1st. Look out the degree 18 (columns 1 and 4) and deduct the tension of aqueous vapour given, = 15·3 mm., from the observed pressure = 742·0 :

$$742·0 - 15·3 = 726·7 \text{ mm.}$$

2nd. Now find the volume which 1 vol. of the gas would have at the pressure of 726·7 mm. by looking out seriatim the figures 7, 2, 6, and 7 in column 2 at the temperature 18°, and placing the numerical values, to be found opposite those figures, in the same column, multiplying them seriatim by 100, 10, 1, 0·1 ; whereupon they are added up, thus :—

$$7 \quad 0 \cdot 0086408 \times 100 \quad = 0 \cdot 86408$$
$$2 \quad 0 \cdot 0024688 \times \ \ 10 \quad = 0 \cdot 024688$$
$$6 \quad 0 \cdot 0074064 \times \ \ \ 1 \quad = 0 \cdot 0074064$$
$$7 \quad 0 \cdot 0085408 \times \ \ \ 0 \cdot 1 = 0 \cdot 00086408$$

$$0 \cdot 89703848$$

3rd. The corrected volume of a cubic centimetre is lastly multiplied by the number of the c. c. previously found; that is in the present case:

$$0 \cdot 89703848 \times 26 \cdot 2 = 23 \cdot 502 \text{ c. c.}$$

Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aqueous vapour in millimetres of mercury for degrees C.
0	1	0·0013157	
0	2	0·0026315	
0	3	0·0039473	
0	4	0·0052631	
0	5	0·0065789	0° = 4·5
0	6	0·0078946	
0	7	0 0092104	
0	8	0·0105262	
0	9	0·0118420	
1	1	0·0013109	
1	2	0·0026219	
1	3	0·0039328	
1	4	0·0052438	
1	5	0·0065548	1° = 4·9
1	6	0·0078657	
1	7	0·0091767	
1	8	0·0104876	
1	9	0·0117986	
2	1	0·0013061	
2	2	0·0026123	
2	3	0·0039184	
2	4	0·0052246	
2	5	0·0065307	2° = 5·2
2	6	0·0078369	
2	7	0·0091430	
2	8	0·0104492	
2	9	0·0117553	

Table (*continued*).

Temperature °C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aqueous vapour in millimetres of mercury for degrees C.
3	1	0·0013013	
3	2	0·0026026	
3	3	0·0039039	
3	4	0·0052053	
3	5	0·0065066	3° = 5·6
3	6	0·0078079	
3	7	0·0091093	
3	8	0·0104106	
3	9	0·0117119	
4	1	0·0012965	
4	2	0·0025930	
4	3	0·0038895	
4	4	0·0051860	
4	5	0·0064825	4° = 6·0
4	6	0·0077790	
4	7	0·0090755	
4	8	0·0103720	
4	9	0·0116685	
5	1	0·0012916	
5	2	0·0025833	
5	3	0·0038750	
5	4	0·0051667	
5	5	0·0064584	5° = 6·5
5	6	0·0077501	
5	7	0·0090418	
5	8	0·0103335	
5	9	0·0116252	
6	1	0·0012868	
6	2	0·0025737	
6	3	0·0038606	
6	4	0·0051474	
6	5	0·0064343	6° = 6·9
6	6	0·0077212	
6	7	0·0090080	
6	8	0·0102949	
6	9	0·0115818	

Table (*continued*).

Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aqueous vapour in millimetres of mercury for degrees C.
7	1	0·0012828	
7	2	0·0025656	
7	3	0·0038484	
7	4	0·0051312	
7	5	0·0064140	7° = 7·4
7	6	0·0076968	
7	7	0·0089796	
7	8	0·0102624	
7	9	0·0115452	
8	1	0·0012783	
8	2	0·0025566	
8	3	0·0038349	
8	4	0·0051132	
8	5	0·0063915	8° = 8·0
8	6	0·0076698	
8	7	0·0089481	
8	8	0·0102264	
8	9	0·0115047	
9	1	0·0012737	
9	2	0·0025474	
9	3	0·0038211	
9	4	0·0050948	
9	5	0·0063685	8° = 8·5
9	6	0·0076422	
9	7	0·0089159	
9	8	0·0101896	
9	9	0·0114633	
10	1	0·0012692	
10	2	0·0025384	
10	3	0·0038076	
10	4	0·0050768	
10	5	0·0063460	10° = 9·1
10	6	0·0076152	
10	7	0·0088844	
10	8	0·0101536	
10	9	0·0114228	

Table (*continued*).

Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aqueous vapour in millimetres of mercury for degrees C.
11	1	0·0012648	
11	2	0·0025296	
11	3	0·0037944	
11	4	0·0050592	
11	5	0·0063240	11° = 9·7
11	6	0·0075888	
11	7	0·0088536	
11	8	0·0101184	
11	9	0·0113832	
12	1	0·0012603	
12	2	0·0025206	
12	3	0·0037809	
12	4	0·0050412	
12	5	0·0063015	12° = 10·4
12	6	0·0075618	
12	7	0·0088221	
12	8	0·0100824	
12	9	0·0113427	
13	1	0·0012559	
13	2	0·0025118	
13	3	0·0037677	
13	4	0·0050236	
13	5	0·0062795	13° = 11·1
13	6	0·0075354	
13	7	0·0087913	
13	8	0·0100472	
13	9	0·0113031	
14	1	0·0012516	
14	2	0·0025032	
14	3	0·0037548	
14	4	0·0050064	
14	5	0·0062580	14° = 11·9
14	6	0·0075096	
14	7	0·0087612	
14	8	0·0100128	
14	9	0·0112644	

Table (*continued*).

Temperature °C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aqueous vapour in millimetres of mercury for degrees C.
15	1	0·0012472	
15	2	0·0024944	
15	3	0·0037416	
15	4	0·0049888	
15	5	0·0062360	15° = 12·7
15	6	0·0074832	
15	7	0·0087304	
15	8	0·0099776	
15	9	0·0112248	
16	1	0·0012429	
16	2	0·0024858	
16	3	0·0037287	
16	4	0·0049716	
16	5	0·0062145	16° = 13·5
16	6	0·0074574	
16	7	0·0087003	
16	8	0·0099432	
16	9	0·0111861	
17	1	0·0012386	
17	2	0·0024772	
17	3	0·0037158	
17	4	0·0049544	
17	5	0·0061930	17° = 14·4
17	6	0·0074316	
17	7	0·0086702	
17	8	0·0099088	
17	9	0·0111474	
18	1	0·0012344	
18	2	0·0024688	
18	3	0·0037032	
18	4	0·0049376	
18	5	0·0061720	18° = 15·3
18	6	0·0074064	
18	7	0·0086408	
18	8	0·0098752	
18	9	0·0111096	

Table (*continued*).

Temperature °C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aqueous vapour in millimetres of mercury for degrees C.
19	1	0·0012301	
19	2	0·0024602	
19	3	0·0036903	
19	4	0·0049204	
19	5	0·0061505	19° = 16·3
19	6	0·0073806	
19	7	0·0086107	
19	8	0·0098408	
19	9	0·0110709	
20	1	0·0012259	
20	2	0·0024518	
20	3	0·0036777	
20	4	0·0049036	
20	5	0·0061295	20° = 17·4
20	6	0·0073554	
20	7	0·0085813	
20	8	0·0098122	
20	9	0·0110331	
21	1	0·0012218	
21	2	0·0024436	
21	3	0·0036654	
21	4	0·0048872	
21	5	0·0061090	21° = 18·5
21	6	0·0073308	
21	7	0·0085526	
21	8	0·0097744	
21	9	0·0109962	
22	1	0·0012176	
22	2	0·0024352	
22	3	0·0036528	
22	4	0·0048704	
22	5	0·0060880	22° = 19·6
22	6	0·0073056	
22	7	0·0085232	
22	8	0·0097408	
22	9	0·0109584	

Table (*continued*).

Temperature °C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aqueous vapour in millimetres of mercury for degrees C.
23	1	0·0012135	
23	2	0·0024270	
23	3	0·0036405	
23	4	0·0048540	
23	5	0·0060675	23° = 20·9
23	6	0·0072810	
23	7	0·0084945	
23	8	0·0097080	
23	9	0·0109215	
24	1	0·0012094	
24	2	0·0024188	
24	3	0·0036282	
24	4	0·0048376	
24	5	0·0060470	24° = 22·2
24	6	0·0072564	
24	7	0·0084658	
24	8	0·0096752	
24	9	0·0108846	
25	1	0·0012054	
25	2	0·0024108	
25	3	0·0036162	
25	4	0·0048216	
25	5	0·0060270	25° = 23·5
25	6	0·0072324	
25	7	0·0084378	
25	8	0·0096432	
25	9	0·0108486	
26	1	0·0012013	
26	2	0·0024026	
26	3	0·0036039	
26	4	0·0048052	
26	5	0·0060065	26° = 25·0
26	6	0·0072078	
26	7	0·0084091	
26	8	0·0096104	
26	9	0·0108117	

Table (*continued*).

Temperature ° C.	Pressure in millims. mercury.	Volume at 0° and 760 mm.	Tension of aqueous vapour in millimetres of mercury for degrees C.
27	1	0·0011973	
27	2	0·0023946	
27	3	0·0035919	
27	4	0·0047892	
27	5	0·0059865	27° = 26·5
27	6	0·0071838	
27	7	0·0083811	
27	8	0·0095784	
27	9	0·0107757	
28	1	0·0011933	
28	2	0·0023866	
28	3	0·0035799	
28	4	0·0047732	
28	5	0·0059665	28° = 28·1
28	6	0·0071598	
28	7	0·0083531	
28	8	0·0095464	
28	9	0·0107397	
29	1	0·0011894	
29	2	0·0023788	
29	3	0·0035682	
29	4	0·0047576	
29	5	0·0059470	29° = 29·8
29	6	0·0071364	
29	7	0·0083258	
29	8	0·0095152	
29	9	0·0107046	
30	1	0·0011855	
30	2	0·0023710	
30	3	0·0035565	
30	4	0·0047420	
30	5	0·0059275	30° = 31·6
30	6	0·0071130	
30	7	0·0082985	
30	8	0·0094840	
30	9	0·0106695	

ALPHABETICAL INDEX.

THE END.

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