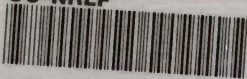# HANDBOOK

OF

TECHNICAL GAS-ANALYSIS.

BY

CLEMENS WINKLER, Ph.D.,

PROFESSOR OF CHEMISTRY AT THE FREIBERG MINING ACADEMY.

SECOND ENGLISH EDITION.

Translated from the Third, greatly enlarged German Edition,
with some additions,

BY

GEORGE LUNGE, Ph.D.,

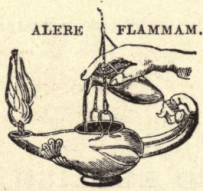PROFESSOR OF TECHNICAL CHEMISTRY AT THE FEDERAL POLYTECHNIC SCHOOL, ZURICH.

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(SUCCESSORS TO JOHN VAN VOORST).

MDCCCCII.

ALERE FLAMMAM.

TRANSLATOR'S PREFACE TO THE FIRST EDITION.

Every one who has to make gas-analyses for technical purposes is aware that Professor Clemens Winkler is the founder of technical gas-analysis as a distinct branch of analytical Chemistry. A few such processes were, of course, previously known and practised; but Winkler was the first to draw attention to the importance of this subject, to invent suitable apparatus, and to elaborate a complete system of qualitative and quantitative technical gas-analysis *, containing a vast number of new observations and methods, along with a very complete description of the work already done in the same direction by others.

The field first opened out by Winkler has been very successfully cultivated by other chemists; and it is now quite usual, at any rate in Germany, to perform technical gas-analyses, not merely in chemical works, but for testing the efficiency of steam-boiler furnaces and such purposes. In England some of these processes have also been introduced; but they are not as yet known and appreciated to the same extent as abroad. Hence it may not be unwelcome to English chemists to have a translation of a short treatise, just published by Winkler, which is primarily intended for *teaching* purposes—that is, for the use of teachers and students in public laboratories—but which likewise serves as a guide and a handy book to other chemists wishing to make themselves acquainted with the subject. This treatise is not intended, as was its predecessor, to furnish a complete enumeration of all apparatus hitherto proposed for technical gas-analysis, but merely to give representative examples of each kind of apparatus, embracing all the divisions of this branch of Chemistry. It may be confidently said that a person who has mastered the processes and apparatus described in this book will at once

* Cl. Winkler, 'Anleitung zur chemischen Untersuchung der Industrie-Gase,' Freiberg, 1877–79 (2 vols.).

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 specially 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.

Zurich, August 1885.

TRANSLATOR'S PREFACE TO THE SECOND ENGLISH EDITION.

THE first edition of the German original of this book appeared in 1884, a second followed in 1892, and a third was published towards the end of 1901. In the meantime the first English edition became exhausted, so that a new issue would have been called for in any case. Professor Winkler kindly consented to allow the Translator to do his work from the proof-sheets of the third German edition, so that this present second English edition corresponds to the third edition of the original.

Although the scope of this work has remained primarily to furnish a help to the *teacher* and the *student* of technical gas-analysis, it has been greatly enlarged, as is proved by the fact that the number of pages has been increased by one-half. It does not even now purport to give a complete enumeration of all processes and apparatus proposed for technical gas-analysis, but it now embraces all the more important of these, including the valuable additions made to that part of technical analysis by Professor Hempel; and it will be found a sufficient guide and help in most cases to the practical and manufacturing chemist, as well as to the student. As before, only methods practically tried and approved by the Author have been recorded in this book.

The Translator has again introduced a few remarks of his own in the text, and has also made some additions describing his own apparatus more fully than is done in the original; but he has taken care to mark everything in such a way that the reader can never be uncertain as regards Professor Winkler's work and the portions added by the Translator.

Zurich, March 1902.

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INTRODUCTION.

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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 *gasvo'umetric* 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 cuprous chloride. 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 volumetric 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

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* Argon and its congeners are never separated from nitrogen in technical analysis.—*Translator*.

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.

The *gravimetrical* estimation of gases is also sometimes performed, in such cases where one of the constituents of a gaseous mixture, which is present only in small quantity, has to be estimated. This supposes that the gas in question can be transformed into a compound of constant composition, capable of being weighed.

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. Combustions by explosion, whether with or without addition of oxyhydrogen gas, should be avoided, if possible. 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 should 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 throughout, and, owing to friction, is

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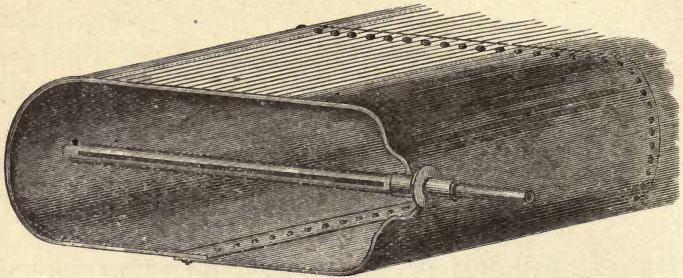
nearest to the aspirator. Up to the present we do not know of any process for taking from a moving current of gas such a sample that it may be said to represent a perfectly correct average of the whole bulk of the gas. But it is possible to come very near the truth by producing a strong *primary current*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

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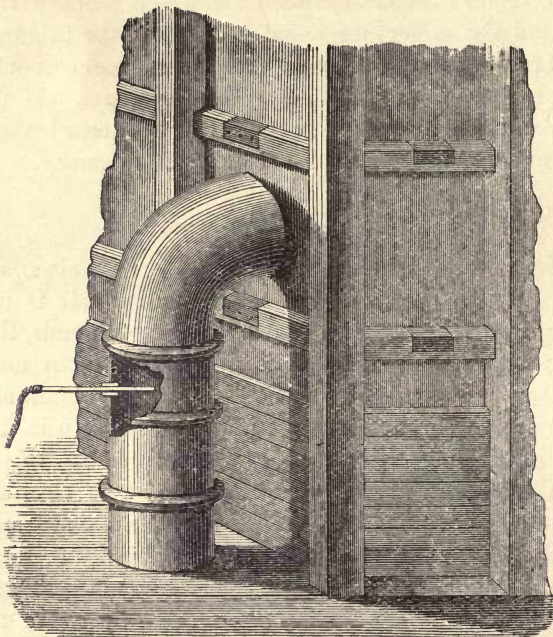
of sampling, and branching off a small *secondary current* from the former by means of a T-pipe, the latter current forming the average sample.

In cases where the composition of the gaseous mixture is subject to frequent and sudden variations (for instance, in furnace-gases, especially from periodically charged fire-places), it is preferable to refrain from collecting an average sample, and in the place of this to take a large number of special samples of the gas, each of which must be analysed separately.

The simplest and safest sampling can be performed with gases stored up in quantity, because these generally get mixed of their own accord by diffusion within the gas-holder *.

The selection of *the place from which the sample is taken* is sometimes a matter of importance. Thus, for instance, the efficiency of an apparatus for absorbing acid gases cannot be accurately ascertained, unless the samples of gas to be examined are taken *before entering the chimney* which forms the final part of the apparatus, since the gas may be diluted within the chimney by air entering from without.

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 to admit of a cork and glass tube being introduced 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

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* It should be observed, however, that this automatic mixture of gases by diffusion cannot be depended upon to take place expeditiously. Occasionally the various layers of gases within a large gas-holder show decided deviating composition for some time after filling the holder.—*Translator.*

porcelain 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
the place where the gas is to be sampled is high enough to soften
glass.   The porcelain tube should be of such a length 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

Fig. 3.
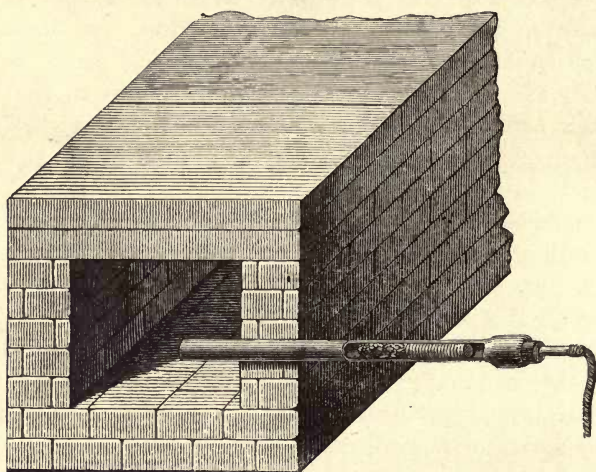
particles (fig. 3).   Porcelain tubes should be gradually heated up,
to prevent their cracking by the heat ; unglazed earthenware pipes,
which are sometimes employed instead, are certainly less sensitive
to changes of temperature, but are not gas-tight, and on this
account cannot be recommended.

   Aspirating-tubes made of metal (iron, brass, copper, silver, pla-
tinum) 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, to provide 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 millims., 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

Fig. 4.
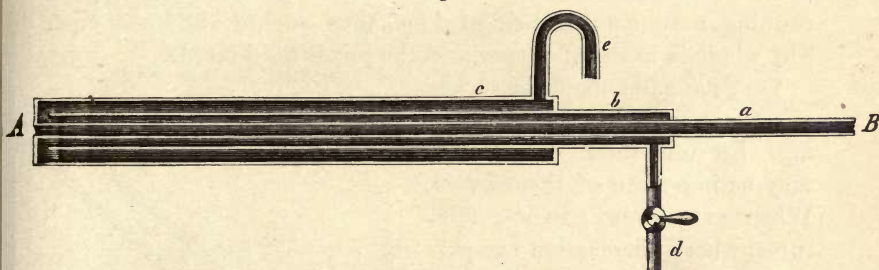
a stopcock, for admitting the cooling water. The outer jacket is formed by the tube c, 20 millims. wide, which at the end A is soldered to the tube a, at the end near B to the tube b. The tube c is also provided with a branch e, through which the cooling water, which has been heated on its way through the tubes b and c, is run off again. The length of the tube AB 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 the apparatus is taken out of the furnace.

A similar, but simplified combination of pipes has been recommended by Drehschmidt (fig. 5). The aspirating-tube a, 4 or 5 millims. wide, is surrounded by a jacket b, closed at both

Fig. 5.
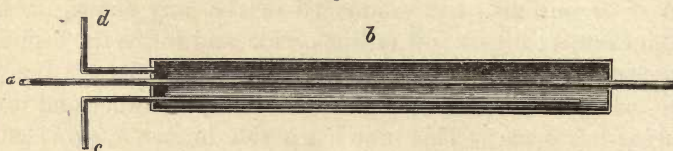
ends, into which cold water is introduced by the supply-pipe c, running away continuously at d and thus cooling the inner pipe. The whole is made of copper and the joints are brazed.

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. 6. The copper tube, 6 to 8 millims. wide, is U-shaped. The part E C, which is intro-

Fig. 6.

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
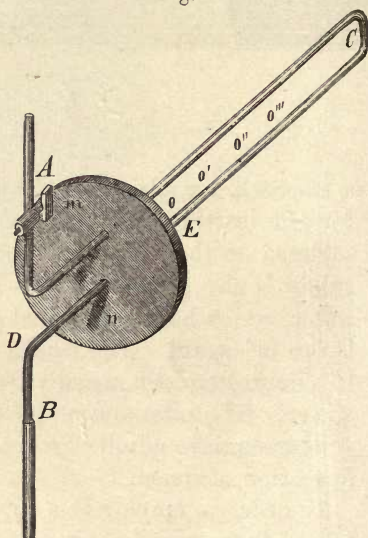
a gas-holder filled with water, where the water and the gas carried away with it are separated. At first a little water squirts out through the saw-cuts, but soon the tube *C D B* begins to act as a siphon, and, if the cock A is set rightly, gas is aspirated through the saw-cuts and collected in the 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. 7.
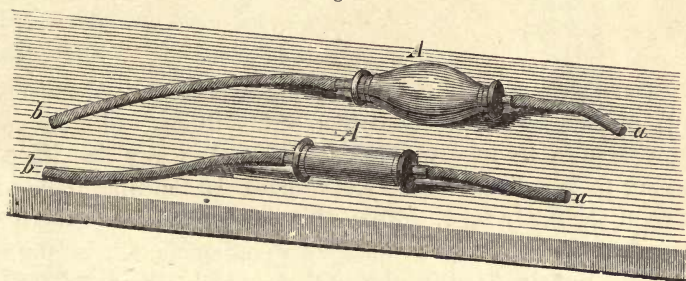
instance, *india-rubber aspirating- and force-pumps* (*hand or foot blowers*) of simple construction, as met with in commerce in various sizes (fig. 7). They consist of a stout vessel *A*, with cylindrical ends, which are stopped up with turned and perforated wooden bungs, provided inside with a very 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. 8). A strong glass tube, about 3 centims. wide, or

Fig. 8.
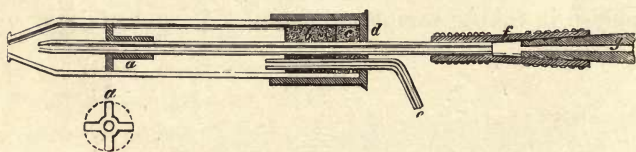
in lieu of this a metallic tube of a length of 20 to 25 centims., is drawn out at one end to an orifice of 6 millims. width ; a steam-pipe is fixed in its longitudinal axis in such a way that its point, tapering to 2 millims. bore, ends about 12 millims. behind the orifice of the outer tube. Near this 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, a considerable number 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 here described.

Fig. 9.

Bunsen's water-air pump * (fig. 9) 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, corresponding 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
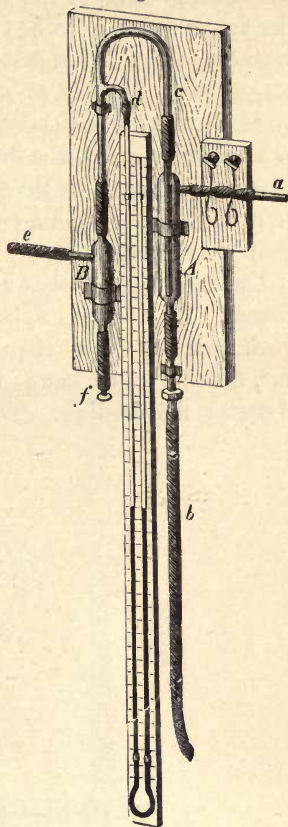
* Really invented by H. Sprengel.—*Translator.*

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 Zulkowsky, 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. 10.
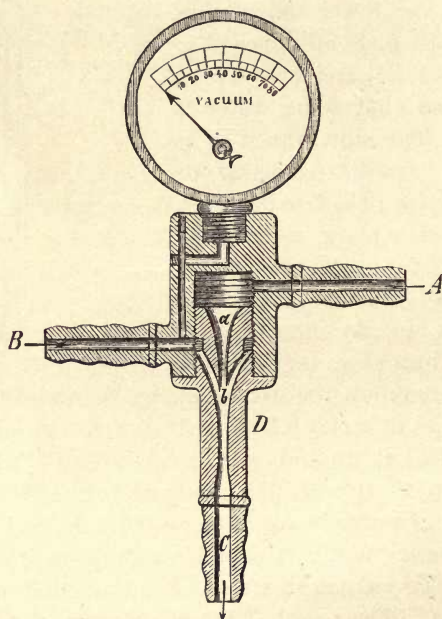
much varied, is apparent from fig. 10.   The water enters at *A*, issues from the conical tube *a*, 1 millim. bore, carries along the air entering through *B*, passes the contracted part *b*, and runs

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* indicates the degree of lessened pressure.

Of a simpler kind but hardly less efficient are the various *water-jet pumps made of glass,* which are found in commerce. These can be connected with any water-tap by means of thick india-rubber tubing; they are easily moved about and are, moreover, deep. To these belongs *Finkener's aspirator* (fig. 11), where the water enters

Fig. 11.   Fig. 12.
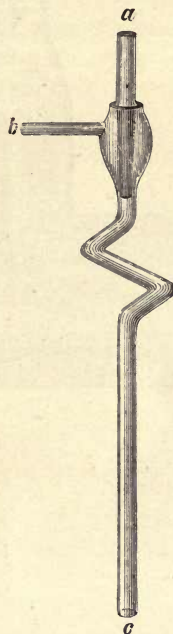
from the service-pipe through the tube *a,* which is drawn out to a point; runs through the tube *c,* which is bell-shaped at the top, contracted in the middle, and again widened at the bottom end; and aspirates air through *b,* which forms a frothy mixture with the water issuing at *c.* In order to diminish the fragility of the apparatus, it is usual to make the lower, tapering tube separate and connect it with the upper part by an elastic joint. Very efficient also are *Geissler's aspirating-tubes,* which can be understood from fig. 12 without special explanation.

Another kind of apparatus admits of both aspirating and collecting 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. 13.
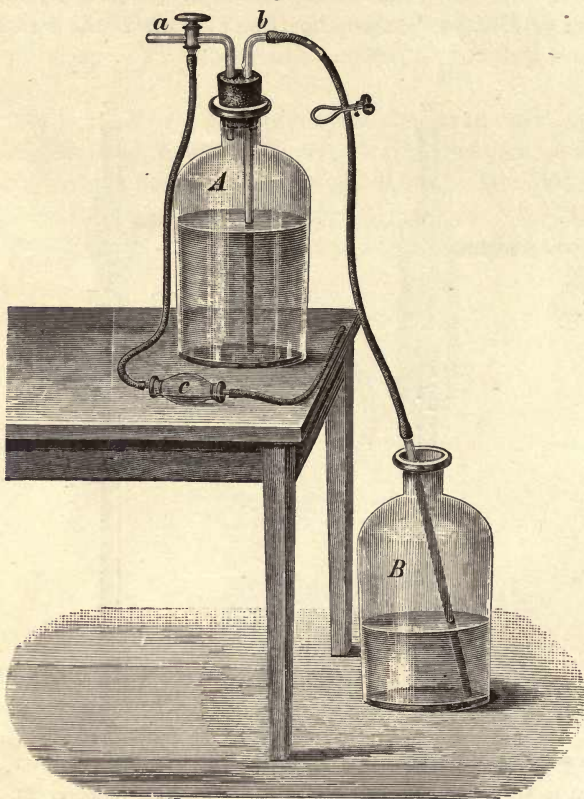
the gas to be examined or after connecting the apparatus with the aspirating-tube.

If somewhat large quantities of gases have to be collected, an *aspirating-bottle,* as represented in fig. 13, 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*. Now by means of the pump *c* all the air is removed from the gas-conducting pipe, after suitably setting the three-way tap; the gas-pipe is connected with *A*, and the gas is aspirated by allowing the water to flow out. Such an arrangement can, for instance, serve in those cases where a reduced sample is to be taken from a main current of gas, aspirated during the whole course of work by means of a water-jet pump. This reduced current should be removed quite as continuously and collected in bottle *A*.

Robert Muencke's double aspirator (fig. 14) 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 brass 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. 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

Fig. 14.
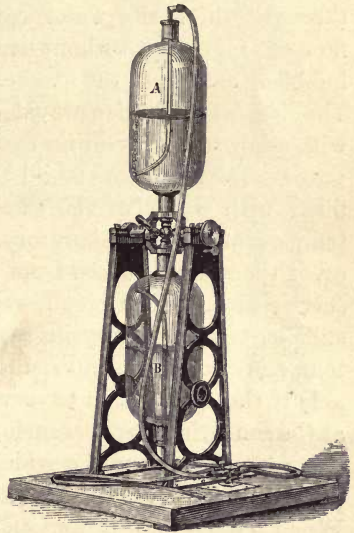
is to be aspirated, and at the same time connects the lower vessel *B*
with the atmosphere.   When the upper vessel is run off, the button
of the spring-arrangement is pressed, the cylinders shifted round the
spindle by 180°, and the lower stopcock turned to the same extent.
In this position the vessel *B* is connected with the gas-apparatus
and *A* with the atmosphere.

Thus this double aspirator per-
mits of almost continuous action
without any change of tubing.

A very convenient form of
zinc aspirators is shown in
fig. 15. The vessel *A*, con-
taining 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 indispens-
able 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 con-
nected by means of an air-tight
screw-socket with a glass T-

Fig. 15.

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
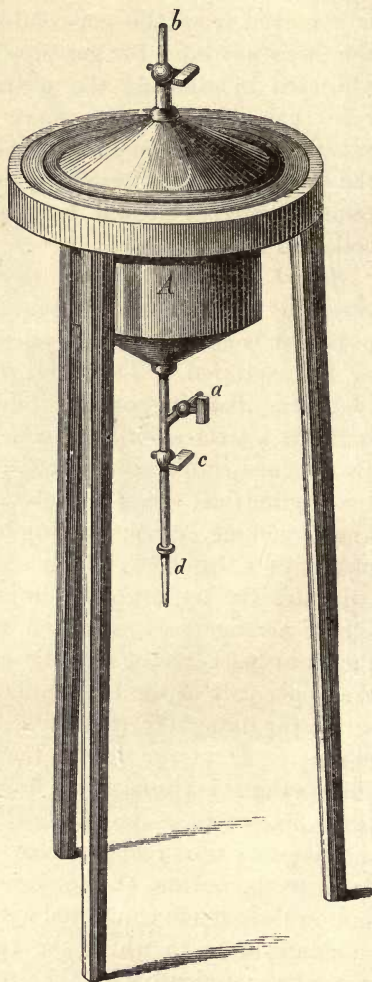
which runs off is collected in a litre-flask placed below. The moment the water in the latter has reached the mark, the tap *c* is closed, but *b* is only closed the moment the pressure-gauge has come to the level again. When this happens a volume of gas exactly equal to that of the water run off has been aspirated.

For aspirating and at the same time measuring large volumes of gas, the *automatic aspirator of J. Bonny* * can be employed. The essential feature of this apparatus (fig. 16) is a metal vessel *A*,

Fig. 16.
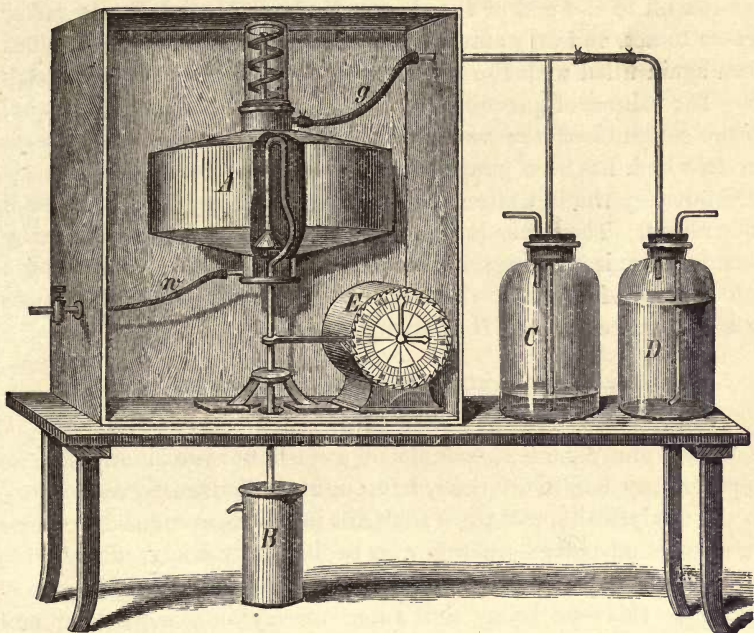
containing on the inside a siphon whose shorter funnel-shaped limb reaches down to the lower part of the vessel, whilst the longer limb is carried through its bottom and dips into the vessel *B*, in which is water at a constant level. Through the india-rubber tube *w*, connected with the water-service, the vessel *A* can be filled with water. The tube *g* serves 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

* Sold by Cornelius Heinz & Co., Aachen: price 75 marks.

c 2

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 should not in any case 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. A rule to be observed in cases where it is unavoidable to employ water-luting is this : to bring the water merely into superficial and momentary contact with the gas, but *never to pass the gas through the water itself*, as is done in a pneumatic trough. Otherwise the solvent action of the water, which is entirely different towards different gaseous substances, would unavoidably alter the composition of the gas to a sensible extent.

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 to entirely 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 should, as a rule, 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. 17 and 18).

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. 19. 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 conveniently 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. 19.
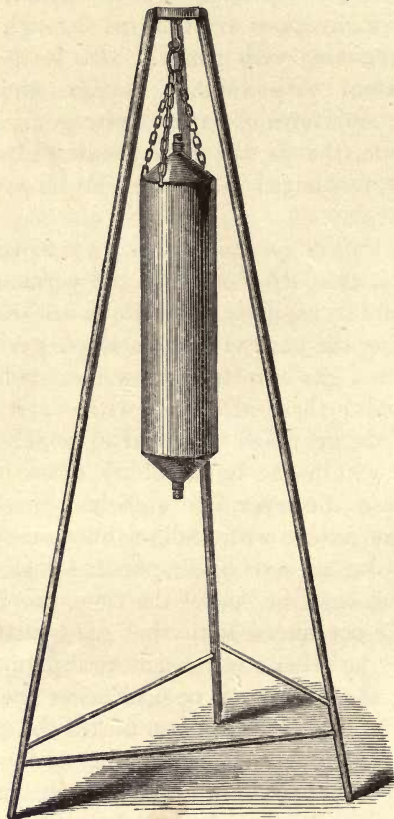
Fig. 18.

Fig. 17.

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 regarded 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. centims. at 0°, it will measure
$273+1$ cub. centims. at 1°; and at t° $273+t$ cub. centims. 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 always takes up 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 tem-
perature, owing to the increased formation and expansion of that
vapour. That tension, expressed in millimetres of mercurial pres-
sure 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 millims. barometric pressure and 20° C. ; its volume in the dry state, at normal pressure and temperature, will be

$$\frac{1000 \times 273 \times (738 - 17\cdot4)}{(273 + 20) \times 760} = 884\cdot4 \text{ cub. centims.}$$

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 gavimetric 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. 20), 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 (fig. 21), 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. 20.
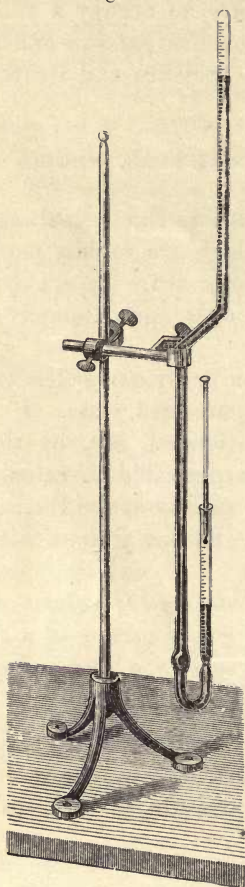
Fig. 21.
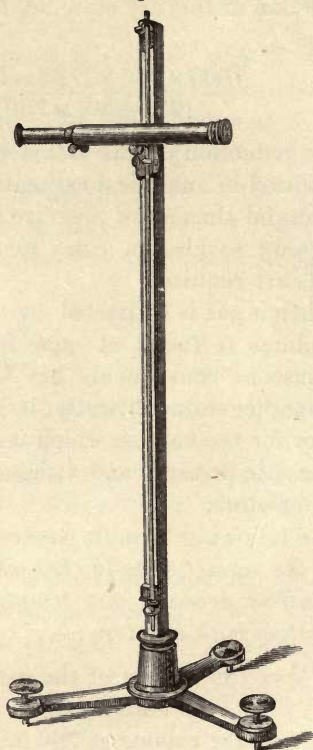
The *temperature* is observed by means of a small thermometer, divided into tenths of a degree, which is loosely placed in the shorter limb of the barometer.

An apparatus for the expeditious reduction of the volumes of gases to the normal state without the necessity of observing the thermometer and barometer was first proposed by U. Kreusler

(Ber. der deutsch. chem. Ges. 1884, xvii. p. 29) and afterwards constructed in a more convenient shape simultaneously by the author (Cl. Winkler, ibid. 1885, xviii. p. 2533) and the translator (G. Lunge, Chemische Industrie, 1885, p. 163). It is shown in fig. 22.

Fig. 22.

An iron stand with two arms carries two perpendicular glass tubes, connected at the bottom by a thick india-rubber tube ; one of these is the measuring-tube, the other the level-tube. The measuring-tube, *A*, is enlarged into a bulb at the top and is closed by a small, slightly greased, and absolutely tight glass tap *. It holds exactly 100 c.c. from the tap to the zero mark ; the division marked on the cylindrical part extends from the zero point to 5 c.c. upwards and 25 c.c. below, so that from 95 to 125 c.c. can be read off accurately to 0·1 c.c. These two extreme values would correspond to 100 c.c. air under normal conditions, saturated with moisture, when brought to 800 mm. B and 0° *t* on the one side, or to 700 mm. B and 30° *t* on the other side, and thus embrace all values occurring under ordinary circumstances. Tube *A* is held vertically in the lower arm of the stand, the division being completely in view.

The level-tube *B* is open at the top, which is protected by a dust-cover. It is held in the lower arm of the stand and can be moved up or down by means of a screw-clamp. It need not hold more than 30 c.c.

In order to set the apparatus once for all for permanent use, a

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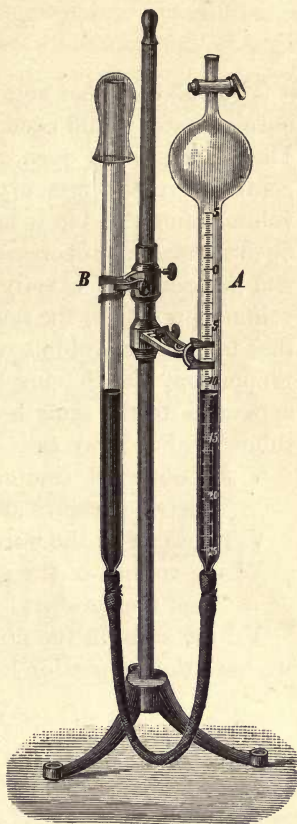
* Experience has shown that no ordinary tap holds tight in the long run the means of attaining this end will be discussed later on, when describing the gas-volumeter.—*Translator*.

few drops of water* are introduced into tube *A,* an approximately sufficient quantity of mercury is poured in, the whole is placed in a cool room, together with a barometer and thermometer, and after a few hours, or better the next day, the state of both the barometer and thermometer is accurately ascertained. According to the formula :

$$V = \frac{100 \times (270 + t) \times 760}{273 \times (B-f)},$$

it is calculated what volume 100 c.c. of air, assumed to be in the normal state, would occupy under the actually existing conditions. The tap being left open, the level-tube is raised or lowered to the point where the mercury level indicates precisely the calculated volume, and the tap is now closed. The volume of air thus confined increases or decreases with every external change of pressure and temperature exactly in the same ratio as another gaseous volume, present in the same room and intended to be measured, so that the normal volume of the latter can be calculated by simple proportion, after having brought the mercury in both limbs of the apparatus to the same level and read off the volume indicated on tube A. For if we call

V the observed volume of air in the tube at the ruling barometric pressure and temperature,

V_0 the same in the normal state (constantly $= 100$),

V^1 the volume of the gas to be examined at the ruling pressure and temperature,

V_0^1 the same in the normal state,

we have the proportion :

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

Compare later on the mechanical reduction by Lunge's gas-volumeter.

G. Lunge has also modified this instrument so as to yield the reduced volume by a simple multiplying operation, and he has described the preparation of such reduction-tubes in a fit state for

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* In those cases where the gas to be measured is sure to be in the dry state, *e. g.* the nitric oxide given off in the analysis of nitrous and nitric compounds by means of the nitrometer, the reduction instrument may be adapted to this special use by putting in a drop of concentrated sulphuric acid, in lieu of water, and calculating accordingly.—*Translator.*

carriage to a distance (Chem. Zeit. 1888, p. 821 ; Zeitsch. f. angew. Chemie, 1890, p. 227) *.

Another correction apparatus is the *Gas-baroscope*, constructed by J. Bodländer, on the principle of gravimetrically estimating the gas (Zeitsch. f. angew. Chemie, 1894, p. 425).

An *approximate correction*, for cases where no great accuracy is required, can be at once made by ascertaining the difference between the volume of a gas in the normal state and that which it possesses under average *local* conditions of pressure and temperature. Thus the yearly average of barometric pressure at Freiberg is 725·6 mm., the mean temperature is 7°·0. 1 c.c. of gas in the normal state, if saturated with moisture, would under these average conditions occupy 1·085 c.c., and an approximate correction would be effected by dividing the read-off volume of gas by the above figure. But we must consider that the temperature of the laboratory is usually above the annual mean, and it is preferable to make the calculation accordingly. Allowing a mean pressure of 725·6 mm. and a temperature of 20°, the correction factor would be 1·135. The real average of observations made in the Freiberg laboratory corresponds to the factor 1·118 †.

I. Direct Volumetrical Estimation.

A. *Measuring in Gas-burettes* (Nitrometer, Ureometer, Gas-volumeters).

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 hydraulically sealed, 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 enlarged into a bulb or a wider cylinder, in order to shorten the tube, which may be useful for practical purposes.

It is unnecessary to say that gas-burettes, as well as all other apparatus serving for gas-analysis, must be correctly gauged and

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* These modifications, as well as the original instrument, have become obsolete by the construction of the gas-volumeter.—*Translator*.

† It is evident that errors up to 10 per cent. may be caused by this method, which consequently can serve only for very rough approximations.—*Translator*.

divided. This may be controlled by the usual methods, or through the Physico-chemical Institute of Dr. Sauer, Dr. Göckel & Co., Berlin W., Wilhelmstrasse 49.

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 background. In the great majority of cases the use of a water-jacket is quite unnecessary, since the water which serves as confining liquid causes a sufficient equalization of temperature *.

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, petroleum, 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. Gniewosz and Walficz (Zsch. f. physik. Chem. i. p. 70) have shown that the absorption coefficient of petroleum for oxygen and other gases greatly exceeds that of water, although Fajans (Chem. Zeit. 1893, p. 1002) held the contrary. 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,

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* This, of course, holds good to a much greater extent as regards the mercury contents of the nitrometer and gas-volumeter, wherefore a water-jacket, which would greatly hamper the manipulation of these instruments, is altogether unnecessary in this case.—*Translator*.

the measuring-vessel proper—with nothing but water if possible. To introduce the absorbing liquids into the burette, as is done in the older kinds 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 $\frac{1}{2}$ 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. It is indispensable that the inner surface of the burette should be clean, especially free from greasy matters, which is secured by rinsing it with caustic potash solution, or preferably with alcohol.

The *reading* itself is taken at the lower concavity of the meniscus of the liquid (fig. 23), 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, p. 26), such as serves for barometrical and thermometrical 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.

Fig. 23.

We shall here describe several apparatus which, ·although

Fig. 24.
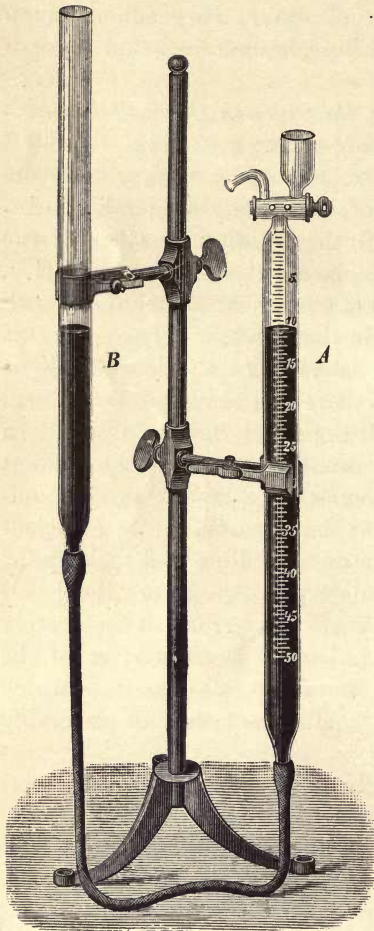
Fig. 25.
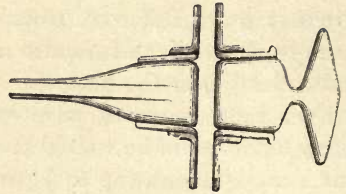
Fig. 26.
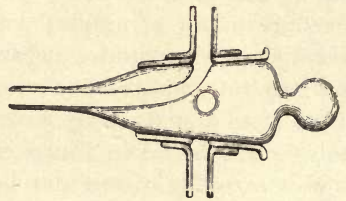
Fig. 27.
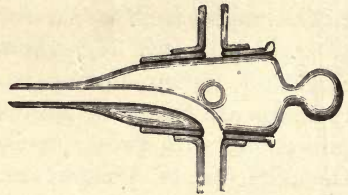
not primarily constructed for gas-analysis proper, can be equally
well applied for this purpose, and which in any case are closely
related to our subject, as they serve for the rapid estimation of

many substances by the measurement of the gaseous products of their decomposition. These are *G. Lunge's Nitrometer, Ureo-meter, and Gas-volumeter* *.

The *Nitrometer* in its original shape †, which is also that best adapted for gas-analysis, is shown in fig. 24 (p. 32). *A* is the " measuring-tube," a kind of gas-burette, fitted at the top with a three-way cock. These cocks, originally constructed, after many laborious attempts, by Cl. Winkler and therefore quite erroneously designated as " Geissler taps," are shown separately in figs. 25 to 30. Figs. 25 to 27 show the original Winkler (or Geissler) shape, where the tap possesses an axial bore, curving sideways so as to issue at right angles with an ordinary cross bore. Another shape of three-way tap has been constructed by Messrs. Greiner & Friedrichs, of Stützerbach, and is shown in figs. 28 to 30. These
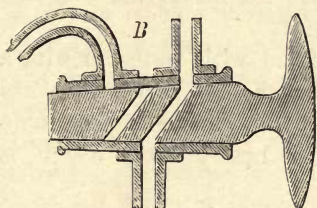
Fig. 28.   Fig. 29.
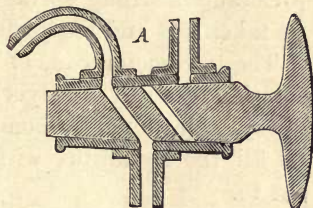
Fig. 30.
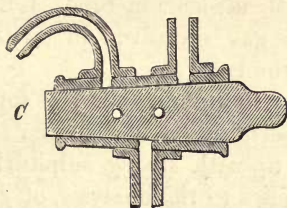
taps, in lieu of the axial and cross bores, possess two slanting bores, and are more easily manipulated and kept tight than the

* The Translator does not in this case, as will be readily excused, simply render the German original into English, but describes the various methods in his own way.

† Ber. d. deutsch. chem. Ges. 1878, xi. p. 434; Chem. Ind. 1886, p. 273.

former construction, wherefore they are preferred by Lunge for his instruments (comp. Zsch. f. analyt. Ch. 1887, p. 49, and Ber. d. deutsch. chem. Ges. 1888, xxi. p. 376).

The tap is surmounted by a cylindrical funnel or cup, visible in fig. 24. Lest the plug of the tap should be thrown out when shaking the instrument, it may be fixed to the narrow part of the funnel by a loop of fine iron or platinum wire (*not* copper wire, which may be acted upon by the mercury unavoidably coming into contact with it).

The measuring-tube is graduated, the zero-point being the upper end adjoining the tap; from this the graduation is continued downwards 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 readjusted in a moment.

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. 30), and it is decidedly preferable to fill the apparatus with mercury for nearly every use it is put to.

Mercury is, of course, indispensable where it has to serve as a reagent in the process; and we shall first of all describe the use of the nitrometer in this instance, where the evolution of gas takes place within the measuring-tube *A* itself, and afterwards those cases where the gas is evolved in an outside vessel and is merely measured in the tube *A.*

The original use of the nitrometer was for *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, including the nitrate, 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 shown in fig. 25 or 28, 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 (fig. 30) so that its vents do not communicate either with the inside or the outside of the tube *A* (comp. fig. 30), 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 seen in fig. 25 or 28, 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 more gas is given off. The 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 6½ 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 a thermometer hung up close by and a barometer, or else the volume of air in the reducing-apparatus (fig. 22, p. 27) 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 contrary takes 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 will be drawn in if the pressure is too low, or raised if it is 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*, thus forcing the gas and all acid into the cup, and put the tap in the position seen in fig. 26, so that the acid flows out and into a vessel placed below ; the last of it is drawn out by blotting-paper.   With the Greiner-Friedrichs tap the acid is not forced back into the cup, but straight out of the tube by means of the position shown in fig. 29.   The nitrometer is then ready for the next experiment.   A test must always be made to ascertain whether the glass tap is air-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 its 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 mg. N_2O_3, or 2.820 mg. 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. 31. 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.

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 gramme.

Put the sample, finely ground if solid, into the tube up to the
mark, cork the tube, weigh it, pour the con-
tents into the cup of the nitrometer, taking
care that the substance settles 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. con-
centrated pure sulphuric acid run in. The
operation is in other respects performed as
described above.

Fig. 31.

The nitrometer should first be tested as to
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.

As an apparatus for gas-analysis proper it is, in most cases, best
to employ the nitrometer fig. 24, p. 32. It is quite evident that
it will fulfil all the functions of Hempel's gas-burette, by attach-
ing to the side-opening of the three-way cock the various pipettes
described later on, 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 nitrometer enjoys a great advan-
tage over Hempel's burette in being filled with mercury, by
admitting of more accurate readings of level, and by being adapted
to the examination of gases partially soluble in water. In some
cases it may serve, like Bunte's gas-burette (comp. later), 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 di-
oxide), or where the reagent required for estimating a second
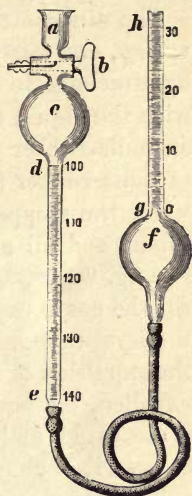
constituent does not interfere with the first, as when we first estimate carbon dioxide by means of caustic potash and subsequently oxygen by pyrogallol.

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 adjusted like fig. 26 or 30, then like fig. 27 or 29. 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. 26 or 30; 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. 31, but that shown in fig. 24 (p. 32). 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 allowing 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.

Another use of the nitrometer is that where the chemical reaction does not take place within the measuring-tube itself, but outside *. Two classes of instruments serve for this purpose, viz.,

* Lunge, Ber. d. deutsch. chem. Ges. 1885, xviii. p. 2030; Zeitsch. f. angew. Chemie, 1890, p. 8.

that provided with a side-flask (for aqueous liquids) and that provided with an agitating-vessel (for reactions with mercury). The former is shown in fig. 32. The *side-flask* or *decomposition-flask*

is provided with an inner tube fused on to its bottom, or (less conveniently, 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 to fill the nitrometer immediately up to the tap, that is to the zero point; it is possible 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

Fig. 32.

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 also 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. These instrument
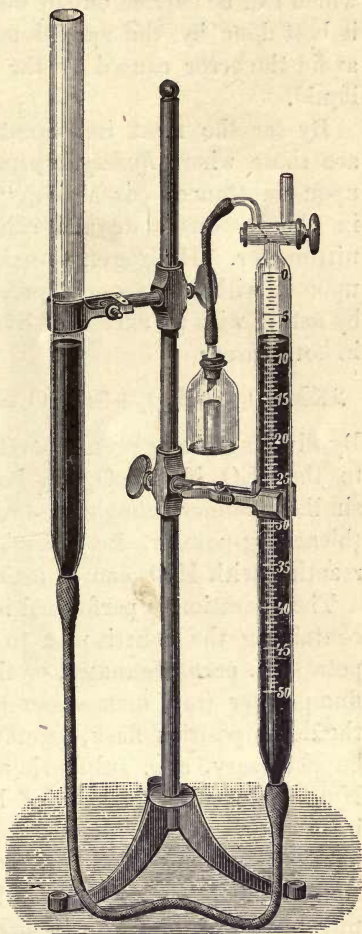
serve, for instance, for the analysis of *ammonium salts* and the estimation of *urea* in urine by means of brominated soda; in the latter case they are called *ureometers*. They may also be used for the estimation of *carbon dioxide* and all the analytical operations which can be carried out by means of such an estimation; but this is best done by the special means to be described below, which avoid the error caused by the solubility of carbon dioxide in the liquid.

By far the most important uses of this shape of nitrometer are those where *hydrogen peroxide* is employed, in order to act upon substances containing "active" oxygen which is set free in the gaseous state and can be accurately measured by the nitrometer. Hydrogen peroxide itself can be analyzed by acting upon it with an excess of *potassium permanganate*, and the latter by acting with an excess of hydrogen peroxide, the reaction being in both cases :

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10\ O.$$
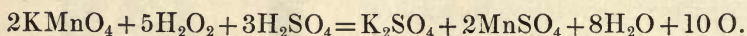
By dividing the oxygen liberated by 2 we obtain that belonging to the H_2O_2 if $KMnO_4$ has been in excess, and *vice versâ*. In a similar manner manganese-ore (essentially MnO_2), hypochlorites (bleaching-powder, &c.), ferricyanides, and all other substances reacting with H_2O_2 can be estimated.

The operation is performed in the following way :—The solution containing the constituent to be estimated (say, a solution of potassium permanganate), or the substance in the shape of a very fine powder (say, manganese-ore), is placed in the *outer* space of the decomposition-flask, together with such other reagents as may be necessary, *e. g.* sulphuric acid in both just-mentioned cases. Now a sufficient quantity of hydrogen peroxide is run into the inner tube. Meanwhile the cork of the decomposition-flask 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; comp. fig. 33. The tap should be turned as in fig. 26 or 28. The cork is now pressed tightly down into the flask, the tap turned as in fig. 27 or 29, 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 adjusted and the volume of gas in the measuring-tube is read off. The reduction

to normal pressure and temperature is effected as prescribed above, p. 26 or 35, or mechanically by the gas-volumeter (see below).

The third method of using the nitrometer is that where a special "agitating-vessel" is used for the reaction of nitrates upon mercury in the presence of sulphuric acid ; but as this is nearly always carried out with a *gas-volumeter*, we shall first proceed to describe this instrument.

Fig. 33.
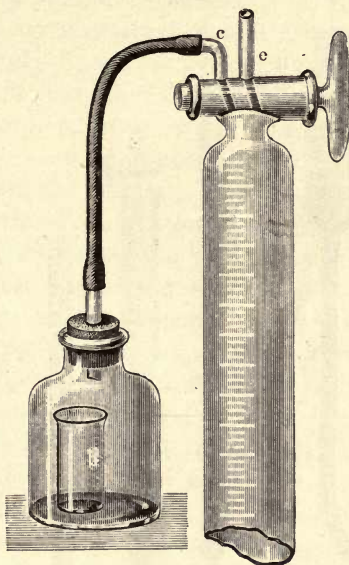
The gas-volumeter * realizes the idea of doing away with all calculations required for reducing a volume of gas to the normal state, by effecting this reduction by a mechanical operation, carried out in a minimum of time and with a maximum of accuracy.

This is brought about by combining the correction-apparatus, fig. 22, p. 27, with a gas-burette, in such manner that both the constant volume of gas contained in the former and the gas contained in the burette are at one and the same time compressed to the volume of 100 c.c. in the former, and therefore equal to the *corrected* volume in the latter. This is performed by combining the three tubes, A, B, C, fig. 34, as follows :—They are all

* Lunge, Berl. Berichte, 1890, xxiii. p. 440, 1892, xxv. p. 3157 ; Zeitsch. f. angew. Ch. 1890, p. 139, 1891, p. 410, 1892, p. 677.

joined by very strong elastic tubing to a three-way pipe D, and they slide upwards and downwards in strong clips. A is the measuring-tube or gas-burette, B the reduction-tube, C the level-tube (all these parts are here shown in their simplest form; they have, however, been considerably improved in shape). A is either

Fig. 34.
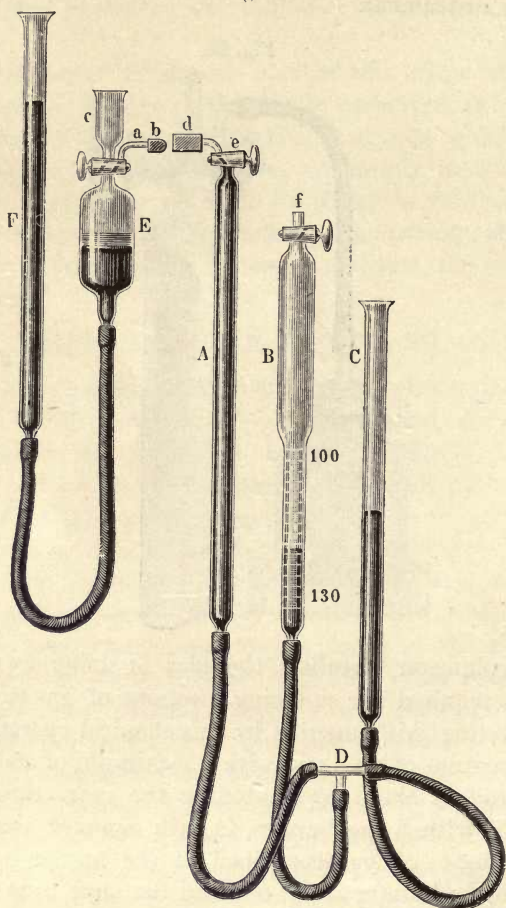
made to hold 50 c.c., divided in 0·1 c.c., or 140 or 150 c.c., the upper 90 or 100 c.c. being formed as a bulb and the graduation being only at 90 or 100 c.c. and reaching down to the bottom; or else the tube has a bulb in the middle, being graduated from 0 to 30, and again from 100 to 150, so as to admit of measuring either

small or large volumes of gas without unduly lengthening the tube. B is made exactly like tube A in the reduction-apparatus, fig. 22, p. 27, and is filled with exactly 100 c.c. air, calculated for 760 mm. pressure and 0°, precisely as stated in that place. But it should be added that this air must be either saturated with moisture, by previously introducing a few drops of water, or else completely dried, by means of a drop of concentrated sulphuric acid. In the first case the instrument is best adapted for the measurement of moist gases, in the second for that of dry gases.

A sufficient quantity of mercury should be previously poured in through the level-tube C, and by means of the latter the mercury is driven up in A till it reaches the tap, whereupon the gas to be measured is either evolved in or carried over into A. In order to measure it in a state reduced to normal conditions, the three tubes are so adjusted that the mercury in B stands at 100 c.c., and at exactly the same level as the mercury in A. It is quite evident that, by doing this, not merely the air contained in B, but also the gas contained in A has been compressed to the point corresponding to 760 mm. pressure and 0° temperature. Thus the reduction of the gas in A to normal conditions is effected without observing the barometer or thermometer, and this is facilitated by special constructions of clamps and stands (comp. Lunge's 'Sulphuric Acid and Alkali,' 2nd edition, vol. ii. p. 113).

The reduction-tube, B, must of course be depended upon not merely to hold exactly 100 c.c. air of 0° and 760 mm., but also to keep this volume entirely unchanged, in spite of the frequent higher or lower pressures to which it is necessarily subjected in the course of the analytical operation. Even the best ordinary glass tap cannot be expected to stand these changes of pressure for any length of time, although it may and should do so for a few hours. Therefore the inventor first recommended to shape he upper end of B so that it could be sealed off at the lamp. As during this operation, in case of unskilful work, an error may be introduced, he substituted for it a special kind of tap, sealed with mercury, as shown in fig. 35. Experience has shown that the volume of air in a reduction-tube provided with this arrange- ment remains unchanged for years; and it is perfectly easy at any time to re-open and close the reduction-tube, if it has got out of order by some extraneous cause. The plug is greased with vaseline, and is kept tight by the mercury at the top even against

strong pressure from either side, especially when kept down on
the top by the cork, as shown in the figure.

Fig. 35.

The gas-volumeter might be used like any
ordinary nitrometer, by introducing the substance
directly into the burette A and developing the
gas within the same. This is, however, not very
convenient; the proper use of the gas-volumeter
is either for operations carried out in a side-
flask (decomposing flask), as described p. 39 *et seq.*;
or, for the analysis of nitrous or nitric com-
pounds by the mercury method, by combination
with two other parts, shown at E and F, fig. 34,
p. 42.

Concerning the former case we have only to
remark that, of course, during the operation of
decomposing permanganate or manganese dioxide
or hypochlorites by hydrogen peroxide, &c., the
level-tube is so placed that no pressure is exerted
on the gas; when the reaction ceases, the mercury
in the gas-burette and that in the level-tube is
placed exactly at the same level, the top of the
burette is closed and only then the mechanical
reduction of the gas contained in the gas-burette is carried out as
described on p. 43.

In the latter case, the mercury in A is first driven up till it just
issues from the side-tube *d*, which is then closed by a short india-
rubber tube and glass rod, the tap *e* being also closed.

Precisely in the same way we treat the agitating-vessel E, by
raising its own level-tube F, so that the mercury is retained in
the side-tube *a* by means of the elastic tube and glass rod *b*. We
now introduce the nitrous vitriol, or solution of sodium nitrate, or
the nitroglycerine, nitrocellulose, &c. into the cup *c*, and transfer
it into the bulb E by cautiously lowering F, just as described on
p. 35. Of course solid nitrate has to be previously dissolved in
the cup *c* by means of a few drops of water, solid gun-cotton &c.
by means of strong sulphuric acid, and so forth, and this is
followed by a sufficient quantity of sulphuric acid for performing
the reaction within E. When this is over and the gas has cooled
down, it is transferred to A for the purpose of being measured.
E is placed in the position shown in the figure, so that the small
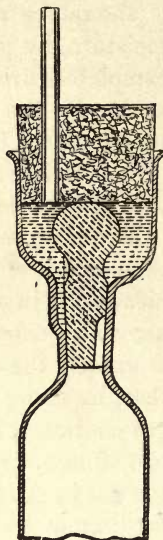
tubes a and d are on the same level. The bits of glass rod are removed and a is pushed into the small piece of elastic tubing fixed on d until the glass tubes touch. Now level-tube C is lowered and F is raised (as shown in the figure), tap c is opened and so is tap e, but quite cautiously. The gas will now be transferred from E into A; at the moment when it has all come over, and when the acid has entered into the bore of e, but before it has got inside of A, tap e is closed. Now the gas in A is compressed by raising tube C to the point where the mercury stands at 100° in B and at the same level in A, as described on p. 43, and the final reading is taken in A.

The readings are greatly facilitated by a brass straight-edge, provided with a spirit-level, as described by Lunge (Berl. Ber. 1891, xxiv. p. 3948).
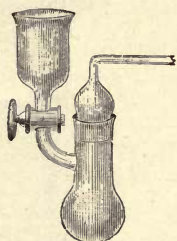
Fig. 35 a.　　　　　　　　　Fig. 35 b.

The principle of the gas-volumeter has been also applied to the exact estimation of carbon dioxide in carbonates, and to that of carbon in iron and steel (Lunge & Marchlewski, Zeitschr. f. angew. Chemie, 1891, pp. 229 & 412), but we cannot discuss this here. We will show only the decomposition-flasks constructed for that purpose, figs. 35 a & 35 b, which admit of heating the contents. Fig. 35 a avoids the use of cork or india-rubber, but is more fragile than fig. 35 b.

B. *Measuring in Gas-meters.*

Gas-meters serve for measuring somewhat large or indefinitely large volumes of gas, and are only rarely used in gas-analysis. 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. 36 and 37) consists of a

Fig. 36.
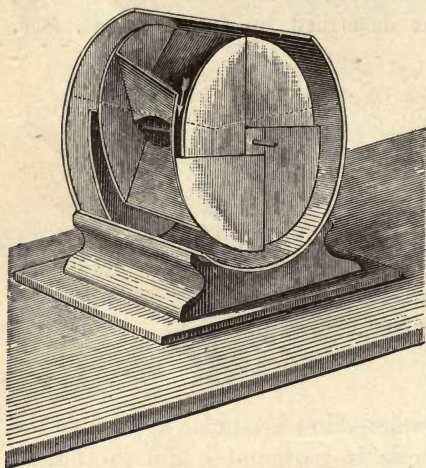
Fig. 37.
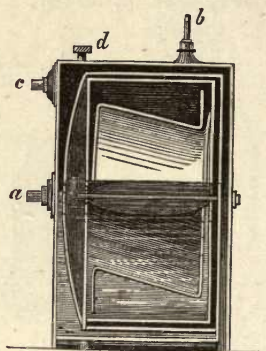
cylindrical sheet-iron vessel, resting horizontally on a base, filled to a little above half its height with liquid (water or glycerine of spec. gravity 1·14), in which moves, about a horizontal spindle, a drum divided by diaphragms into several chambers of exactly equal capacity.   There are usually 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. At the Berlin gas-works 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.

Where the same kind of work frequently recurs, consisting in the estimation of a constituent of a gas occurring in minute quantities, *e. g.* ammonia in illuminating-gas, it is preferable to work always under the same conditions, and therefore also to employ the same volume of gas for every estimation. In such cases the outlet of the gas is regulated by means of a tap provided with a micrometer-screw. But as the quantity of gas to be employed is usually large and the time required for passing it through is considerable, it is desirable to possess a gas-meter which is automatically stopped after a certain quantity of gas has passed through. Tieftrunk (Verh. d. Ver. z. Beförd. d. Gewerbfl. 1876, xxxix. 5th appendix) has described such an *automatically stopped gas-meter* where, after the passage of 100 litres of gas, the index uncouples a lever and thus shuts the tap.

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, and supplied by L. A. Riedinger, of Augsburg. These meters pass a maximum of 500 or 600 litres per hour. Their dial is provided with two hands, one of which (the smaller) is fixed to the spindle of the drum and moves along with it, indicating

the smaller divisions. This hand 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 $\frac{1}{10}$, $\frac{1}{50}$, $\frac{1}{250}$, 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. centims., can be read off with certainty.

Every gas-meter should 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 at the end of the experiments.

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 1 c.c. corresponds to exactly 1 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 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, to which the caoutchouc cork which serves for closing it is pressed down. This cork has two perforations, usually closed with pieces 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. 38). 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. 38.
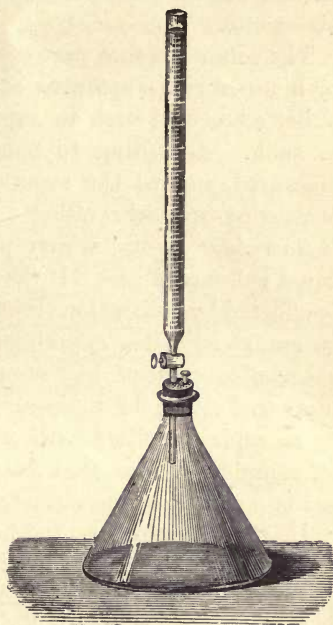
On the same principle are founded those methods by which the gas under examination is measured in a gas-meter, and is afterwards passed through an absorbing-vessel charged with a measured excess of standard absorbing-liquid.

E

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 direct, 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 atmo-

sphere, 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 the purpose.

III. Gravimetrical Estimations.

A. *Gravimetrical Analysis.*

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 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 Sect. II., 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.

B. *Estimation of Specific Gravity.*

In many cases the specific gravity of gaseous mixtures admits of drawing a conclusion as to their composition. In the manufacture of illuminating-gas, for instance, where very different products are formed in various stages of the process, that estimation is universally performed. It can also be made available for judging the quality of furnace-gases, of pyrites-kiln gases, and similar cases. In technical examination the following two methods are principally employed :—

a. *Estimation of the specific gravity of a gas by measuring its velocity when issuing from an orifice.*

The weight of two gases which under equal conditions issue from an orifice is approximately in the same proportion as the squares of the time of the outflow. If a gas of specific gravity s possesses the outflowing-time t and another of specific gravity s_1 the outflowing-time t_1, the relation between the outflowing-time and the specific gravities is

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

If the unit of comparison is atmospheric air with the specific gravity $s = 1$, the specific gravity of the other gas is found by the formula

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

This principle was first employed by Bunsen ('Gasometrische Methoden,' 2nd edition, p. 184) for estimating the specific gravity of gases. H. N. Schilling (Handb. d. Steinkohlengas-Beleuchtung, 3rd edition, p. 100) has since constructed a convenient apparatus for the estimation of the specific gravity, in the first instance of coal-gas, but equally applicable to all other gases or gaseous mixtures sparingly soluble in water.

Schilling's apparatus, as shown in fig. 39, consists of a cylindrical glass tube, A, 40 mm. wide inside, and 450 mm. long. Its upper end is cemented into a brass cover through which passes the inlet-pipe a, and which in its centre carries the outlet-pipe b. A thermometer also passes through the cover. The inlet-pipe a is a brass tube, 3 mm. wide, turning outside in a right angle and provided with a stopcock; it is connected with the source of the gas by an elastic tube. The outlet-pipe b is 12 mm. wide, and is closed at the top by a piece of platinum foil. In the centre of this foil a small orifice is made by means of a very fine needle, and is afterwards hammered out; and this forms the orifice for the issue of the gas. Tube b has a tap, shutting off the connection between the cylinder and the orifice. $B\,B$ is a wider cylinder (125 mm. wide),

Fig. 39.
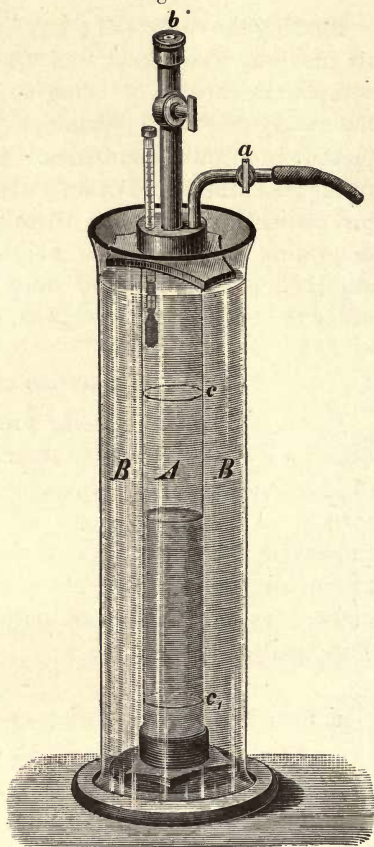
filled with so much water that this reaches nearly to the top when the inner cylinder, filled with air or gas, is immersed in it. This height of water is shown by a mark in the glass. The inner cylinder has two marks, c and c_1, running all round, 300 mm. distant from each other, while c_1 is 60 mm. distant from the bottom of the cylinder A. This cylinder is open at the bottom and is provided with a metal foot serving as guide.

In order to determine the outflowing-time, and thereby the specific gravity, of a gas by means of this apparatus, we must first know what time is required for a volume of air confined in cylinder A between marks c and c_1 to issue through the orifice of the platinum-foil. Fill cylinder B with water up to the mark and then introduce A, which is open at the bottom and filled with atmospheric air, in a vertical position, until the water reaches a little below mark c_1. Now the top of b is opened and sufficient air is allowed to escape through the upper orifice, until the water in A stands exactly at mark c_1. At this moment a seconds-watch or seconds-pendulum is observed, and the air is allowed to issue from b until the water has reached the upper mark c, which will take place in about 4 minutes. The requisite time is exactly observed, and the number of seconds noted.

The procedure is exactly as described if it is desired to determine the specific gravity of the gas to be examined. Cylinder A is filled with the gas through tap a, after having temporarily lifted it up in the confining water; it is emptied again through tap b, and this filling and emptying is several times repeated until all the air previously contained in the cylinder is completely removed. Then it is adjusted to mark c_1 and the gas is allowed to issue as before through the orifice in the platinum-foil until the water has risen to mark c, noting again the number of seconds required for that purpose.

Suppose we have worked first with air, then with carbon dioxide, and we have found the time of outflow—

With air .... = 285 seconds (t),
,, carbon dioxide ...... = 360 ,, (t_1).

According to the above formula there is :

$$s_1 = \frac{t_1{}^2}{t^2} = \frac{129600}{81225} = 1\cdot596.$$

This is the specific gravity of pure carbon dioxide : hence the gas employed contained 100 per cent. CO_2.

Suppose we have to examine in the same manner a mixture of air and carbon dioxide. The outflowing-times are :

$$\text{Air} \dots\dots\dots\dots\dots \quad 285 \text{ seconds } (t),$$
$$\text{Gaseous mixture}\dots\dots \quad 305 \quad ,, \quad (t_1).$$

$$s_1 = \frac{t_1^2}{t_1} = \frac{93025}{81225} = 1 \cdot 145.$$

If we call d the difference between the specific gravity of carbon dioxide and air, d_1 that between the specific gravities of the gaseous mixture examined and air, the expression

$$\frac{d_1 \times 100}{d}$$

must give the percentage of carbon dioxide in the gaseous mixture, or in our case :

$$\frac{d_1 \times 100}{d} = \frac{(1 \cdot 145 - 1 \cdot 000)\,100}{1 \cdot 596 - 1 \cdot 000} = 24 \cdot 3 \text{ per cent. } CO_2 \text{ by volume.}$$

b. *Estimation of the specific gravity of a gas by direct weighing with employment of a gas-balance (densimetric method of gas-analysis).*

The direct weighing of gases is performed by the gas-balance of Friedrich Lux, of Ludwigshafen-am-Rhein (fig. 40). It possesses a beam, one side of which is formed by a gas-pipe which admits of filling, through the axis, a glass ball of 2 litres capacity surrounding the pipe. The other branch of the beam is finished off as an index, with balance-weight, and pointing to a scale. The gas to be weighed can be continuously passed into the glass ball by an elastic tube and continuously extracted in the same way. When filling the ball with air, it takes a certain position, which, by moving the balance-weight, can be made to coincide with point 1 of the scale. If a heavier gas enters the ball, this side of the beam will become heavier and sink ; if a lighter gas enters, this side of the beam will rise. The index must always make the inverse motion, and the difference of weight which has been produced can be read off directly on the scale.

Lux's gas-balance was, like Schilling's apparatus, destined in the first instance for controlling the specific gravity of illumi-

nating-gas, and practically serves almost exclusively for this purpose. There is, however, no reason why it should not be employed for ascertaining the quality of other gaseous mixtures, as fuel-gases, roasting-gases, lime-kiln gases, and thus controlling the state of work. In all these cases the gases should be continuously passed through the glass ball, and as the proper conditions of work are at the outset known to correspond to a certain state of the index, any greater deviations from these conditions would be at once observed.

Fig. 40.
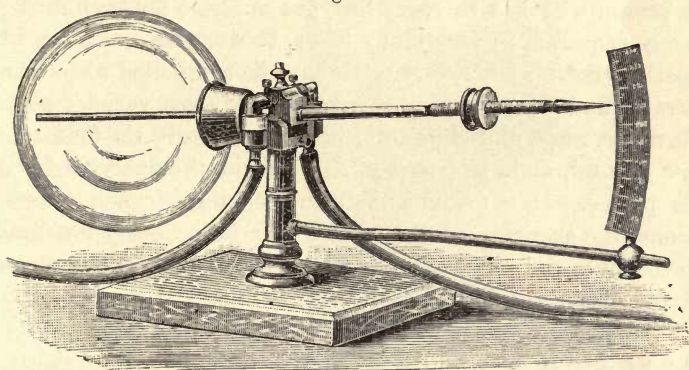
This principle has been utilized, especially for the control of furnace fires, by special instruments called "dasymeters" or "econometers" (for instance, Arndt's econometer, sold by Jos. Wilkes, 41 Holzmarkt, Cologne). In this case the gases must be first deprived of soot and moisture and cooled down to the ordinary temperature before entering into the apparatus, which is usually graduated so as to show directly the percentage of CO_2 in the gases. This system offers, in fact, a very good check upon the way in which the stoker serves the fire, and is frequently employed in factories for that purpose.

Lux has also proposed a densimetric method of gas-analysis. He first finds the specific gravity of a gaseous mixture (s_1), then removes a certain constituent (s_2) by a suitable absorbent, and ascertains the specific gravity of the residual gas (s_3) by a

second gas-balance.   In this case the proportion of the constituent removed by absorption is :—

$$x = \frac{s_1 - s_3}{s_2 - s_3}.$$

This might be followed by absorbing a second constituent and examining the residual gas by a third gas-balance, and so on. This method does not seem to have acquired much practical application.

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 should give a good light and 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. Hempel proposes to heat the room by means of a sheet-iron pipe, placed on the floor in the middle of the room, which rises at one end near the wall and passes out near the ceiling.   Two gas-burners suffice for heating the opposite ends, and a small gas-jet in the vertical part of the pipe serves for aspirating air through it. That portion of the pipe which is less than hand-warm is preferably

made of paste-board, which resists the chemical action of the gases better than sheet-iron. This suffices for a room of 2000 cubic feet capacity.

The temperature of the apparatus, the reagents, the water, and the absorbing-liquids must 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.

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-

Fig. 41.
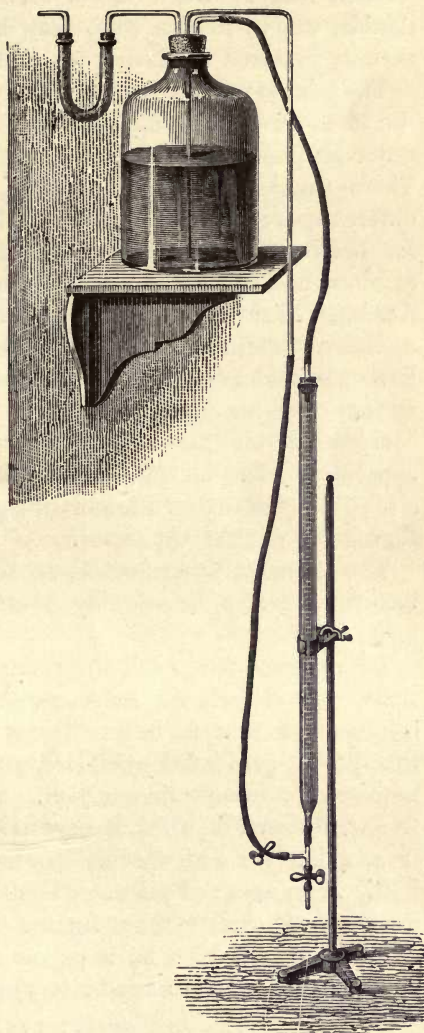
pieces and junctions, pinch-cocks, test-papers, and so forth.   Some small tables are surrounded with a bevelled wooden ledge; they are made to shelve towards the centre, and a circular hole is made in the deepest place, in which a glass funnel and down-pipe are fixed. The top of the table is afterwards 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 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 litres capacity, and are conducted to the various working-places.   There is likewise a pipe for supplying compressed air for use in the combustion- and absorption-apparatus.   The air of the laboratory itself sometimes contains a sensible quantity of illuminating-gas *, and should not be used for rinsing out the apparatus.

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

Besides measuring- and absorbing-apparatus of various construc-tions, 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. 41) will make this arrangement clear without further description.

There should also be a galvanic battery or other source of electricity (*e. g.*, a storage-battery) and an induction-coil.

* This surely ought not to happen!—*Translator.*

CHAPTER III.

APPARATUS AND METHODS FOR CARRYING OUT THE ANALYSIS OF GASES.

I. ESTIMATION OF SOLID AND LIQUID ADMIXTURES.

THE gases to be examined, especially those which occur in the practice of factories, do not always consist of gases alone. They frequently contain solid or liquid substances mechanically carried along, which can be retained by rest, filtration, or washing. The liquid admixtures are always accompanied by vapours of the same substance.

Although in many cases the presence of such substances in a gas does not sensibly influence its volume, and therewith the results of gasvolumetric analysis, it may be desirable to remove them and at the same time to estimate their quantity. Both of these functions are usually performed at the same time as taking the samples of the gas, of course followed by measuring the gas drawn off. If, as is frequently the case, it is necessary to employ a comparatively large volume of gas merely for the purpose here mentioned this is measured by a gas-meter, or else by means of an aspirator based on the outflowing of water. The meter or aspirator always forms the final portion of the analytical apparatus.

Solid admixtures frequently, *e. g.* in smoke or furnace-gases, consist merely of *soot*; in other cases of *dust* of extremely varying composition—*e. g.*, minerals, metals, colouring-matters, fibres, flour, coal, gunpowder. In the *flue-dust* from metallurgical operations there are found the oxides, sulphides, sulphates, chlorides, sometimes the iodides of various metals.

The quantity of *dust* contained in a gas may vary between great

limits.   Thus Fodor found in the street-air of Budapest, 15 feet above the street level :—

in winter	0·00024	gram dust per cubic metre ;
„ spring	0·00035	„	„	„
„ summer	0·00055	„	„	„
„ autumn	0·C0043	„	„	„

The air of Paris, according to Tissandier, contained after a week's dry weather 0·0230, after heavy rain 0·0060 gram dust per cubic metre.

Hesse found per cubic metre air from a living-room and nursery 0·0016 gram, from the rag-picking shop of a paper-works 0·0229 gram, from the cleaning-room of a foundry 0·1000 gram dust.

Stapff found in 1 cubic metre air from the St. Gothard Tunnel, during the time it was constructed, from 0·375 to 0·873 gram dust.   Stöckmann found in 1 cubic metre blast-furnace gas 1·900 grams ; Theisen, in the same, before washing, 3·340 grams, after washing 0·010 gram dust.   Scheurer-Kestner found in chimney-gases from a coal fire, when strongly firing 0·22C9 gram, when damping the fire 0·9649 gram carbon as soot.   Krause found in 1 cubic metre air of a phosphorus-matches factory, 0·004 to 0·005 gram phosphorus.   F. Blum has published a pamphlet (Frankfurt-a.-M., 1900) on the causes of lead intoxication, in which a method for estimating the lead dust contained in the air is described (p. 9).

Sometimes very large quantities of air have to be employed for estimating the dust, especially where not merely its quantity has to be ascertained, but also sufficient material must be collected for a microscopical and chemical examination, for the purpose of determining the hygienic properties, or the value or the inflammability of the dust.   The latter, as is well known, exerts great influence in the case of explosions in coal-pits and flour-mills.

The retention of solid substances mixed with a gas in the shape of dust is performed by filtration.   Even very small particles, such as occur in smoke, of 0·0C02 to 0·C03 mm. diameter, can be retained by means of a suitable filtering-medium, with sufficient filtering-surface and not too rapid a current of gas.   Carded cotton-wool is very efficient : where this is not possible to use, as with acid gases, we may take gun-cotton or soft, curly glass-wool.   This material is placed in an ordinary calcium-chloride tube, and is

dried by exposing the tube in an air- or water-box at 100° to a current of dry air, until the weight remains constant. This tube is interposed between the place where the gas is withdrawn and the aspirator or meter, a suitable volume of gas (up to 1 cubic metre per 24 hours) is drawn through it more or less quickly, the tube is dried again at 100°, and the increase of weight ascertained. If the collected dust, which is principally found at the entrance, is to be chemically examined, this can be done by the ordinary analytical methods. O. Brunck describes filtering-tubes for collecting the dust from coal-pits exposed to fire-damp, which are provided with ground-on glass caps, and admit of weighing the dust with its natural moisture. They are carried about in boxes lined with cork slabs, of such size that the caps cannot fall off.

In order to ascertain the quantity of *soot in furnace-gases* (chimney-smoke), a known volume of smoke is drawn through a tube of refractory glass, containing an asbestos layer, 20 cm. long. The soot is afterwards burned in a current of oxygen, and the carbon dioxide absorbed in potash bulbs, as in elementary analysis, of course interposing a calcium-chloride tube before the potash bulbs.

P. Fritzsche (Zsch. d. Ver. deutscher Ingenieure, 1897, p. 885) describes a colorimetric test for the *smoke-density of chimney-gases* caused by soot. It is founded on the more or less pronounced grey colour of a filtering-medium, consisting of cellulose fibre, afterwards shaken up with a certain volume of water, and comparing it with the colour of paper tinted by Indian ink.

H. Wislicenus (Zsch. f. angew. Chem. 1901, p. 689) makes an approximate examination of forest air suspected of being contaminated by soot, by exposing to it frames covered with thin calico, and comparing the degree of blackening produced after a certain time.

In gaseous heating- and illuminating-materials we always find *naphthalene*-vapours, which up to the present cannot be estimated with any degree of accuracy. But, according to Tieftrunck, their quantity is closely connected with that of the ammonia contained in the gas, and both rise and fall at the same time, although in an unknown relation. Hence the estimation of ammonia in such gases affords a rough idea of the naphthalene they contain.

Liquid admixtures in gases occur mostly in the shape of vapour;

but if the sample has been taken in the hot state, the liquid may be partially condensed by cooling. This condensation is never sufficiently complete to admit of an estimation of the substance; it should be always combined with an absorption- or washing-process in order to ascertain the total quantity of the substance in question.

Water is estimated by absorption in a weighed calcium-chloride tube. If the gas contains ammonia, the best drying-agent is that employed by Stas, and recently again recommended by C. Frenzel (Zsch. f. Elektrochemie, 1900, p. 486), which is obtained by heating a mixture of 3 parts of finely divided copper and 1 part of potassium nitrate in an iron crucible to a strong red heat.

Mercury (of which Janda found 0·00875 gram per cubic metre in the principal chimney of the Idria quicksilver works) is found by interposing a weighed tube filled with gold-foil, and re-weighing after the passage of the gas.

Sulphuric acid, occurring as such or as *sulphur trioxide,* together with sulphur dioxide, in roasting-kiln gases, is found by estimating the total acids (comp. below) and subtracting the sulphur dioxide titrated in another portion.

The estimation of *carbon disulphide* in air has been described by Biehringer (Dingler's Pol. Journal, cclxxvi. p. 78), Schmitz-Dumont (Chem. Zeit. 1897, pp. 487 & 510), Goldberg (Zeitsch. f. angew. Ch. 1899, p. 75), but their methods do not seem to have found much application in gas-analysis. Nor do we know of any practical employment of Eiloart's assertion (Chem. News, lii. p. 184), according to which the vapour of carbon disulphide can be removed from a gaseous current by iodine, or else by absorption with linseed-oil and volumetrical estimation. In illuminating-gas carbon disulphide never occurs alone, but always together with *mustard-oil, mercaptane,* and other organic sulphur compounds. These may be either transformed altogether into the easily absorbable hydrogen sulphide (comp. this), or we may content ourselves with ascertaining the total sulphur in the gas (comp. this), including the hydrogen sulphide.

The quantity of *tar* contained in a gas can be retained and weighed by interposing a glass tube filled with loose cotton-wool. More accurate is its estimation by means of an apparatus constructed by Tieftrunck, in which the gas is thoroughly washed

with alcohol of 25 to 30 per cent. by weight. The alcoholic solution is allowed to evaporate in a weighed vessel at the ordinary temperature; to the weight of the residue one-third is added, which, according to experience, corresponds to the light tar-oils evaporating at the same time, especially benzene and toluene. The latter, as well as other low-boiling hydrocarbons formed in the destructive distillation of coal, are estimated by absorbing them in fuming sulphuric acid, as will be described in the case of ethylene.

Hempel & Dennis (Ber. d. deutsch. chem. Ges. 1891, xxiv. p. 1162) have worked out a method for estimating the *hydrocarbon vapours* in coal-gas. They first pass the gas into a gas-burette, where it is measured, and from this into a gas-pipette filled with mercury, say, an explosion-pipette (comp. later on), where it is shaken up for three minutes with 1 c.c. of absolute alcohol. The gas, thus freed from hydrocarbon vapours, is carried back into the burette, and from this, in order to remove the alcohol vapours, into a second mercury pipette, where it is shaken up for three minutes with 1 c.c. of water, after which the contraction of volume is noted. Both alcohol and water should first be saturated with coal-gas. Comp. on this subject, F. Fischer, Zsch. f. angew. Ch. 1897, p. 349.

In order to estimate *benzene occurring together with ethylene* and other hydrocarbons absorbed by fuming sulphuric acid, Drehschmidt and, later on, Harbeck & Lunge (Zsch. f. anorgan. Chem. 1898, xvi. p. 26; comp. also Lunge & Akunoff, ibid. 1900, xxiv. p. 191) have tried to utilize the property of ethylene (first observed by P. van Wilde) to combine with hydrogen in the presence of platinum-black, by which it is transformed into non-absorbable ethane. But as this process does not take place in the presence of carbon monoxide (which forms a compound with platinum), and as the gases in question nearly always contain that substance, this method is only exceptionally applicable.

Harbeck & Lunge (Zsch. anorg. Ch. xvi. p. 16) describe a *gravimetric estimation of benzene*, founded on transforming the benzene vapour contained in the gas by means of a mixture of fuming nitric acid and sulphuric acid into dinitrobenzene, which can be weighed as such. This method requires about 10 litres of gas and a somewhat complicated apparatus, so that it is not very convenient for ordinary

use, but very suitable for controlling other methods.   O. Pfeiffer (Lunge's Chemisch-technische Untersuchungsmethoden, vol. ii. p. 595) has slightly simplified that method.

Haber & Oechelhäuser (Ber. d. deutsch. chem. Ges. xxix. p. 2700; comp. Haber, Journ. f. Gasbeleucht. 1900) absorb first benzene and ethylene at the same time by means of fuming sulphuric acid, and in another sample of the gas they titrate ethylene by bromine vapour, benzene vapour being indifferent to bromine vapour.   Comp. *infrà*, p. 67.

E. Müller (Journ. f. Gasbeleucht. 1898, p. 433) absorbs benzene, according to Bunte's proposal, by cooled paraffin-oil, spec. grav. 0·88–0·89, boiling at 360°.   The gas, dried by calcium chloride, is passed through four absorbing-vessels, cooled with ice and salt, placed in series and connected so that glass touches glass*, in a slow current, say 2 c.c. per second.   The absorbed portion is found by re-weighing the absorbers, after having taken the temperature of the room; the non-absorbed portion is measured in a gas-meter.   This process is employed at coke-works for the estimation of the benzene contained in the gases, which on the large scale is recovered by a precisely similar process.

Ferro-carbonyl, which occurs in slight quantities in water-gas (Roscoe & Scudder found 2·40 grams Fe in 1 cb. metre of gas), is estimated by passing a known volume of water-gas through a refractory glass tube, heated to red heat; here metallic iron is deposited as a dark mirror.   Another portion of the iron is carried away by the gaseous current in the shape of dust, and is retained by a cotton-wool plug placed in the end of the tube.   The iron is then dissolved in dilute sulphuric acid and titrated.   In a similar way *nickel carbonyl* might be estimated.

Nitroglycerine in the shape of vesicular dust is formed during blasting-operations with dynamite and causes headache and other troubles.   It may be absorbed from the air by alcohol and estimated by evaporation at ordinary temperatures; but practical experience on this point is still lacking.

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* According to my experience this precaution does not prevent the benzene from being partly absorbed by the india-rubber joints.—*Translator*.

II. Estimation of Gases by Absorption.

1. Direct Gasvolumetric Estimation.

A. *Absorbing-agents for Gases.*

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

The *absorbing-agents* are nearly always employed in solution, frequently in a somewhat concentrated state, especially when they have to be used over and over again. The continuous employment of the same absorbing-liquid nearly up to exhaustion is to be recommended, because even those gases which are not absorbable by a chemical reaction are mechanically dissolved to a sensible extent in aqueous liquids. Consequently, when employing a freshly prepared absorbing-liquid, the percentage of the absorbable gas is found rather too high, and this error is only absent when the liquid has been saturated with the mechanically dissolved gases.

We quote here the following absorbents for various gases and their preparation.

a. *Absorbents for Carbon dioxide.*

Carbon dioxide is easily and rapidly eliminated by a solution of *potassium hydroxide.* Dissolve 250 grams good commercial caustic potash, but not specially purified by alcohol, in water and dilute to 1 litre. 1 c.c. of this potash liquor usually contains about 0·21 gram real KOH and consequently absorbs 0·083 gram $= 42$ c.c. CO_2. The absorption is always finished in one minute, usually in a shorter time; it is quite unnecessary to allow ten minutes for it, as has been recommended.

For some purposes, *e. g.* for use in Bunte's burette, the liquor need not possess the above concentration. In other cases, *e. g.* with Orsat's apparatus, it may be used in a more concentrated state; but the higher its concentration, the greater its viscosity and its action on the glass vessels.

A solution of caustic potash serves also for absorbing other acid gases, as *chlorine, hydrogen chloride, hydrogen sulphide, sulphur*

F

dioxide, &c. Caustic soda has the same action, but acts more strongly on glass, and is therefore less to be recommended.

b. *Absorbents for heavy Hydrocarbons.*

The heavy hydrocarbons to be taken into consideration in technical analysis belong to the following classes :—*Olefins,* $C_n H_{2n}$, especially *ethylene,* $C_2 H_4$, small quantities of *propylene,* $C_3 H_6$, and *butylene,* $C_4 H_8$; then the hydrocarbons of the series $C_n H_{2n-2}$, of which *acetylene,* $C_2 H_2$, is the principal representative ; and lastly the *benzenoid* hydrocarbons, $C_n H_{2n-6}$, principally *benzene,* $C_6 H_6$, and *toluene,* $C_7 H_8$. As regards the occurrence of these hydrocarbons in coal-gas as the illuminating constituents proper, they and their determination have lost much of their importance through the introduction of the Welsbach light. They are estimated absorptiometrically by means of the following reagents :—

1. *Fuming sulphuric acid,* usually of spec. grav. 1·938, and containing about 24 per cent. free SO_3.—Below 15° crystals of pyrosulphuric acid are formed. This agent absorbs all the heavy hydrocarbons to be considered here, if agitated with them during five minutes. *Ethylene* is in this case converted into ethionic acid, $C_2 H_6 S_2 O_7$, *acetylene* into acetylenesulphuric acid, $C_2 H_4 SO_4$, *benzene* into benzenesulphonic acid, $C_6 H_6 SO_3$. J. Schroeter (Ber. d. deutsch. chem. Ges. 1898, xxxi. 2189) states that fuming sulphuric acid with acetylene does not form acetylenesulphuric acid, but methionic acid, $CH_4 S_2 O_6$; but this is not the case, at least not under the conditions present in gas-analytical operations, for this would involve the formation of carbon monoxide, which does not take place. In contradiction to that statement, the acetylene is completely absorbed, as confirmed by Knorri & Arndt (Verh. Gewerbfleiss, 1900, p. 166).

The absorption is carried out in a simple Hempel's gas-pipette (comp. this), of course being very careful in filling it ; it is closed by a small glass rod, enlarged at one end, or a glass cap, in order to prevent the attraction of moisture. These need not be taken off during use. Hempel recommends to provide this pipette with an additional bulb above the ordinary ones, filled with bits of glass, in order to enlarge the absorbing surface and to render any agitation unnecessary. After absorption the acid vapours contained in the gas must be removed from it by means of a potash pipette.

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

By this agent only the *totality of heavy hydrocarbons* present in a gas can be estimated, but this is done with sufficient accuracy. The attempts at *separating* the single members have not met with much success. Concerning benzene, comp. *suprà*, p. 63. Fritzche (Zsch. f. angew. Chem. 1896, p. 456) proposes to estimate *ethylene* by itself by diluting its solution in fuming sulphuric acid with water and distilling off the ethylic alcohol formed. He also states that *butylene* and *ethylene* can be separated by means of sulphuric acid, spec. grav. $1\cdot620 = 70$ per cent. H_2SO_4, which dissolves only butylene, not ethylene.

According to E. St. Claire Deville (Journ. des Usines à Gaz, 1889, p. 13), the benzene contained in a sample of gas is to some extent taken up by the confining water and by the potash solution employed for absorbing the carbon dioxide, and the same holds good of other gases and vapours (comp. p. 65). In the case of coal-gas analyses the error thus caused is usually eliminated by first shaking up all the liquids with coal-gas; but it can be directly ascertained by first estimating CO_2 by absorption *plus* the C_6H_6 taken up at the same time, and in a second sample titrating the CO_2, which shows the amount of absorbed benzene-vapour by difference.

2. *Bromine water.*—Saturated bromine water is diluted with two volumes of water, so that the liquid contains about 1 per cent. bromine. It gives off sufficient bromine vapour to impart to the gas in contact with it a yellow colour. It is kept in a composite Hempel's pipette, provided with a water seal. It quickly transforms *ethylene* and its homologues into bromides, without the necessity of agitation. As Treadwell & Stokes (Ber. d. deutsch. chem. Ges. 1888, xxi. p. 3131) and Haber & Oechelhäuser (ibid. 1896, xxix. p. 2700) have found, the absorption is complete, but the employment of bromine water always involves the removal of the bromine vapours from the residual gas by a potash pipette.

Acetylene behaves like ethylene. *Benzene* the author has found (Zsch. f. analyt. Chem. 1889, p. 285) to be but slowly and incompletely removed. Haber & Oechelhäuser (*loc. cit.*) ascertained that this removal takes place not by chemical action, but

mechanically; when benzene vapour and bromine vapour are in contact during two minutes in diffused daylight, no bromine is consumed. Hence it is impossible to carry out the gas-volumetrical separation of benzene from the other heavy hydrocarbons by this agent; but the quantity of benzene can be ascertained by first absorbing the totality of heavy hydrocarbons by means of fuming sulphuric acid, then treating a second sample of gas with bromine water, and determining the consumption of bromine by means of potassium iodide and sodium thiosulphate.

c. *Absorbents for Oxygen.*

Only a few of the numerous agents proposed for the absorptiometric estimation of oxygen have in the long run proved satisfactory. Thus, e. g., *chromium protochloride*, proposed by von der Pfirdten (Ann. Chem. ccxxviii. p. 112), obtained by dissolving chromium acetate in hydrochloric acid, is certainly efficient, but more troublesome to prepare and to employ than other agents. De Koninck (Zsch. f. angew. Chem. 1890, p. 727) proposed an alkaline solution of *ferrous tartrate*, but this is less effective than other agents.

The following substances can be recommended as thoroughly tested :—

1. *Phosphorus.*—It is moulded into thin sticks by melting it in a glass cylinder under warm water so as to form a layer 10 or 15 cm. deep, dipping into this a glass tube of 2 or 3 millimetres bore, closing this at the top with the finger and quickly transferring it into a vessel filled with cold water. As the phosphorus solidifies, its volume shrinks so that the stick can be easily pushed out under water, especially if the glass tube is slightly conical. With a little practice a large number of thin phosphorus sticks are prepared in this manner, and these are ultimately cut into smaller pieces under water. Phosphorus can also be obtained in this shape from the dealers in chemicals.

The phosphorus is placed in a suitable vessel, *e. g.* a Hempel's tubulated pipette, completely covered with water and protected against light. The water serves as a seal ; if it is driven out by the gas to be examined, the latter comes into contact with the moist phosphorus and the absorption of oxygen begins at once, with formation of white clouds of phosphorous acid, which render the gas opaque for some time without influencing its volume. If

the absorption takes place in a dark room, a bright light is produced whose vanishing, as well as the clearing away of the cloud, marks the end of the process. About two or at most three minutes' quiet contact of the gas with moist phosphorus is ordinarily sufficient for the absorption of oxygen. 1 gram phosphorus when transformed into phosphorous acid takes up $0\cdot77$ gram $= 538$ c.c. oxygen; hence the stock of phosphorus contained in one of the absorbing-vessels generally lasts for years. The water covering the phosphorus, which is gradually transformed into a solution of phosphorous and phosphoric acid, should be renewed from time to time.

Certain circumstances influence the absorption of oxygen by phosphorus, viz. :—

(a) *The temperature.* At $18°$ or $20°$ the absorption proceeds satisfactorily; between $12°$ and $17°$ it is very slow and it ceases almost entirely at $7°$. Hence the phosphorus pipettes during the cold season should be brought to a medium temperature before use.

(b) *The partial pressure of oxygen.* Pure oxygen at the pressure of an atmosphere is not absorbed by phosphorus at a temperature not exceeding $23°$. The absorption begins only when the gas has been reduced by means of the air-pump to about 75 per cent. of the initial pressure; it may then set in with extreme violence, up to the production of scintillations and to the melting of the phosphorus. If, therefore, a gas rich in oxygen, *e. g.* commercial compressed oxygen itself, has to be examined, the gas should be diluted with its own volume of pure nitrogen, which may be taken out of a phosphorus pipette filled with air.

(c) *The presence of certain gases and vapours* retards or even stops in a hitherto unexplained way the oxidizing action of oxygen on phosphorus. Perhaps this phenomenon is of a similar kind to the " paralyzing " action of minute quantities of hydrogen sulphide, carbon disulphide, and other foreign substances upon the catalytic action of platinum and of organic ferments, as observed by Bredig and Müller von Berneck (Zsch. f. physik. Chem. 1899, p. 324).

Among the substances interfering with the absorption of oxygen by phosphorus are, according to Davy, Graham, and Vogel, hydrogen phosphide, hydrogen sulphide, sulphur dioxide, carbon disulphide, iodine, bromine, chlorine, nitrogen peroxide, ethylene, acetylene, ether, alcohol, petroleum, oil of turpentine, eupion, creosote, benzene, tar, and many essential oils. How strong this

influence may be is shown by the fact that as little as $\frac{1}{1000}$ vol. PH_3, $\frac{1}{400}$ vol. C_2H_4, $\frac{1}{4444}$ vol. oil of turpentine suffices for making phosphorus and oxygen indifferent to each other. Hence the application of phosphorus as an absorbent for oxygen is restricted, and is excluded in all cases where the presence of such disturbing substances is to be assumed with any degree of certainty. But, according to experiments made by O. Brunck at Freiberg, these substances can in most practically occurring cases be removed by a previous treatment of the gas with fuming sulphuric acid, so that this enables the analyses of illuminating-gas and that of fire-damp to be made by that means. This proves the incorrectness of the assumption hitherto held, according to which methane and ethane belong to the class of interfering substances, as these are not removed by the treatment with fuming sulphuric acid.

The method in question renders excellent service in the examination of air, of chimney-gas, vitriol-chamber gases, &c.; for, generally speaking, phosphorus is superior as to certainty and speed of action to every other reagent for the absorption of oxygen. Lindemann (Zsch. f. analyt. Chem. 1879, p. 158) has greatly facilitated the practical use of this reagent by the construction of a special absorbing-apparatus.

(d) *The presence of combustible gases.* E. Baumann (Ber. d. deutsch. chem. Ges. 1883, xvi. p. 2146) and Leeds (Chem. News, xlviii. p. 25) state that carbon monoxide in the presence of oxygen in contact with moist phosphorus is partially oxidized into carbon dioxide. This has been contradicted by Remsen & Keiser (Amer. Chem. Journ. 1883, p. 454); but Baumann maintains his position (Berichte, 1884, xvii. p. 283). Boussingault has also shown (Compt. rend. lviii. p. 777) that during the slow combustion of phosphorus in gases containing oxygen a small portion of any combustible gases present, as carbon monoxide or hydrogen, vanishes together with the oxygen; but this simultaneous combustion is comparatively slow and, at least in technical gas-analysis, causes no sensible error.

2. *Alkaline solution of pyrogallol.*—An aqueous solution of pyrogallol in contact with air changes but very slowly, but on addition of an alkali it rapidly absorbs oxygen and takes first a red, afterwards a deep brown colour. According to Liebig (Ann. Chem. Pharm. lxxvii. p. 107) 1 gram pyrogallol, with addition of potash solution, absorbs 189·8 c.c. oxygen; according to

Doebereiner (Gilb. Ann. lxxii. p. 203, lxxiv. p. 410) on addition of ammonia 266 c.c. oxygen. The latter statement agrees with experiments made by P. Mann in the author's laboratory, where 1 gram pyrogallol dissolved in 20 c.c. caustic potash solution of spec. grav. 1·166 absorbed 265·2 to 278·7 c.c. (on the average 268·9 c.c.) oxygen.

This behaviour of pyrogallol was first utilized for the eudiometric estimation of the oxygen in atmospheric air by Chevreul in 1820, and was further investigated by Liebig. Weyl and Zeitler (Ann. Chem. Pharm. ccv. p. 255) showed that the absorbing action of pyrogallol is a function of the alkalinity of the solution, but that in too highly concentrated solutions of potassium hydrate the absorbing power is weakened, probably by partial decomposition of the pyrogallol. A solution of KOH of spec. grav. 1·05 was found suitable, 1·50 was too strong. The author's experiments have shown that a solution of caustic potash of spec. grav. 1·166, as employed for the absorption of carbon dioxide, is very suitable indeed, if 50 grams pyrogallol are added to 1 litre. 1 c.c. of this solution absorbs 13 c.c. oxygen. Caustic potash purified by alcohol should not be employed in this case. The absorption of oxygen takes place more slowly than that of carbon dioxide, but it is usually complete within three minutes, if the gas and liquor are brought into very intimate contact and if the temperature does not fall below 15°. The solution is kept in a composite gas-pipette.

Boussingault (Compt. rend. lvii. p. 885) and, later on, Calvert and Cloëz (ibid. pp. 870 & 875) have shown that during the oxidation of the alkaline solution of pyrogallol a small quantity of carbon monoxide may be formed. The quantity of this gas is not constant, but is dependent upon the energy of the absorbing process. Pure oxygen yields more carbon monoxide than if diluted with nitrogen or otherwise ; the formation of carbon monoxide is also favoured by the concentration of the absorbent. From 100 vols. pure oxygen Boussingault obtained 3·4—1·02— 0·40—0·06, Calvert 1·99—4·00, Cloëz 3·50; from 100 vols. oxygen mixed with various proportions of nitrogen, Boussingault obtained 0·40, Cloëz 2·59 vols. carbon monoxide. Consequently Boussingault states that, when applying this absorbent to the examination of atmospheric air, it may happen that the volume of oxygen is found 0·1 or 0·2, or even 0·4 per cent. below the truth.

Vivian B. Lewes (Journ. Soc. Chem. Ind. 1891, p. 407) recommends
to employ the solution not more than four times, as it only then
begins to yield carbon monoxide.   He also recommends to keep it
for twelve hours before use, but he gives no reason for this.
Contrary to the afore-mentioned statements, Poleck (Zeitsch. f.
analyt. Chem. 1869, p. 451), when specially examining this source
of error in researches on the composition of air, could not find
even traces of carbon monoxide to be formed by the employment
of pyrogallol, and he therefore recommends this method as per-
fectly reliable in the case of moderate percentages of oxygen.
The same observation is made in technical gas-analysis; at all
events the quantity of carbon monoxide evolved is too small to
sensibly influence the results of determinations of oxygen.

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

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

Copper moistened with liquor ammoniæ absorbs oxygen much
more quickly than the alkaline solution of pyrogallol, and more
conveniently, as there is no necessity for agitation.   Its efficiency
is nearly equal to that of phosphorus, but it is superior to the

latter as being absolutely harmless and as being active down to $-7°$ C. But its use is restricted by the fact that it absorbs equally well carbon monoxide, which is present in many gaseous mixtures where oxygen must be determined. It also absorbs ethylene and acetylene, the latter with formation of red, explosive copper acetylide. Before employing it, carbon dioxide must of course be removed.

d. Absorbents for Carbon monoxide.

The general absorbing-agent for carbon monoxide is a solution of *cuprous chloride,* which absorbs it with formation of carbonyl-cuprous chloride, $Cu_2 \begin{smallmatrix} -Cl_2 \\ -CO \end{smallmatrix}$. It may be employed both as a solution in hydrochloric acid or in ammonia; but the latter is now generally preferred, because the carbon monoxide absorbed by it in the presence of an excess of ammonia is gradually used up for the formation of ammonium carbonate, and at the same time metallic copper is deposited on the sides of the absorbing-vessel. This reaction is formulated thus:

$$Cu_2(Cl_2.CO) + 4NH_3 + 2H_2O = 2Cu + 2NH_4Cl + (NH_4)_2CO_3.$$
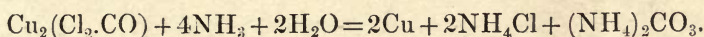
By this reaction the absorbed carbon monoxide is removed again, and on the other hand the free copper protects the solution against oxidation and reduces any cupric chloride formed to cuprous chloride.

A very suitable solution of cuprous chloride, sufficiently ammoniacal, with but slight vapour-tension, is prepared as follows:—250 grams ammonium chloride is dissolved in 750 c.c. water in a bottle provided with a good india-rubber cork and 200 grams cuprous chloride is added. The latter on frequent agitation dissolves, leaving a little cupric oxychloride behind, forming a brown liquid which keeps for an indefinite time, especially if a copper spiral is inserted, reaching from top to bottom. In contact with air the solution forms a precipitate of green cupric oxychloride. In order to make it ready for use, it is mixed with one-third its volume of liquor ammoniae, spec. grav. $0·910$. It is usually kept in Hempel pipettes with a water seal, provided at the lowest point of the connecting-tube with a short branch tube, fitted with a pinch-cock, to facilitate the charging. This is performed by connecting the open end of the pinch-cock tube with an india-rubber tube reaching above the top of the pipette, putting a funnel into the top, and pouring in first 50 c.c. liquor

ammoniæ and then 150 c.c. of the stock solution of cuprous chloride, whereupon the charging-tube is taken off and the outer end of the pinch-cock tube is closed by a bit of glass rod.

1 c.c. of this ammoniacal cuprous chloride solution absorbs 16 c.c. CO. But as this gas is held so loosely that the combination is destroyed to a slight extent even by a decrease of pressure, as found by Tamm (Jernkontorets Annaler, vol. xxxv.) and Drehschmidt (Berichte, 1887, xx. p. 2752), the latter recommends (ibid. 1888, xxi. p. 2158) to employ two pipettes in series— the first, which has to receive the bulk of the carbon monoxide, charged with a cuprous chloride solution used several times previously ; the second, which has to absorb the small remainder of carbon monoxide, charged with a fresh, very active, solution. These two pipettes should be provided with labels of different colour, to prevent mistakes.

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

Sometimes it is sufficient merely to *prove the presence of carbon monoxide by a qualitative reaction,* in such cases where there is too little of it for a gasvolumetrical estimation, and where its combustion to carbon dioxide and gravimetrical estimation in this shape is not possible on account of the presence of other carbon compounds. This is, for instance, the case with the air of heated rooms and of certain coal-pits. In such cases a *colorimetrical* test can be applied (Ch. Winkler, Zeitsch. f. analyt. Chemie, 1889, p. 275) by absorbing the carbon monoxide in a suitable solution of cuprous chloride, diluting and adding sodium-palladium protochloride. The absorbent is prepared by dissolving 100 grams Cu_2Cl_2 in 1 litre of nearly saturated sodium chloride solution. This solution is colourless or but slightly brownish ; it forms a precipitate of green cupric oxychloride in contact with air, but keeps unchanged in a bottle closed with an india-rubber cork and provided with a copper spiral reaching from top to bottom. If the gas is slowly passed through this solution, or agitated with it in a closed bottle for some little time, most of the carbon monoxide is absorbed. A portion of the liquid is put into a test-tube, diluted with three or four volumes of water, without troubling about the white precipitate of cuprous chloride (this is indispensable !), and

a drop of a solution of sodium-palladium protochloride is added. In the presence of the slightest quantity of carbon monoxide a black cloud of finely divided palladium is formed. If the test is always performed under exactly similar circumstances, the depth of the black colour admits of approximately guessing the quantity of carbon monoxide. Thus 0·01 c.c. of $CO = 0·0000125$ gram can be found. The presence of other gases does not materially influence the reliability or sensibility of this reaction.

e. *Absorbents for Nitrogen.*

These may be used for the isolation of *argon* and its congeners. Hempel (Zeitsch. f. anorgan. Chem. 1899, xxi. p. 19) has proved that nitrogen is absorbed at a red heat by a mixture of 1 part (by weight) magnesium powder, 5 parts freshly ignited calcium oxide, and 0·25 part sodium. 1 gram of this mixture during an hour absorbed 52 c.c. nitrogen.

B. *Estimation of Gases by means of Apparatus combining the functions of Absorption and Measuring.*

A description of these apparatus and methods might be considered superfluous, as regards the apparatus described below under *a*, because they have been replaced by better ones of late years. Nevertheless this description will not be omitted, both because these apparatus and methods give an idea of the gradual evolution of technical gas-analysis, and because they are persistently employed in many places up to this day, in spite of all progress made elsewhere. Moreover, their manipulation is an excellent help in teaching, as they make the student quickly familiar with the physical principles to be applied in the measurement of gases.

a. WINKLER'S GAS-BURETTE.

The apparatus described below, constructed by the author in 1872, consists of two communicating tubes, the measuring-tube *A* (fig. 42) and the level-tube *B*, held by the clamps of an iron stand, and 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 as described above (p. 33; see figs. 25, 26, 27). 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. 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 *e*, 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, the apparatus is placed on a lead-covered wooden basin *C*, provided for the (mostly alkaline) absorbing-liquids and rinsings.

Fig. 42.
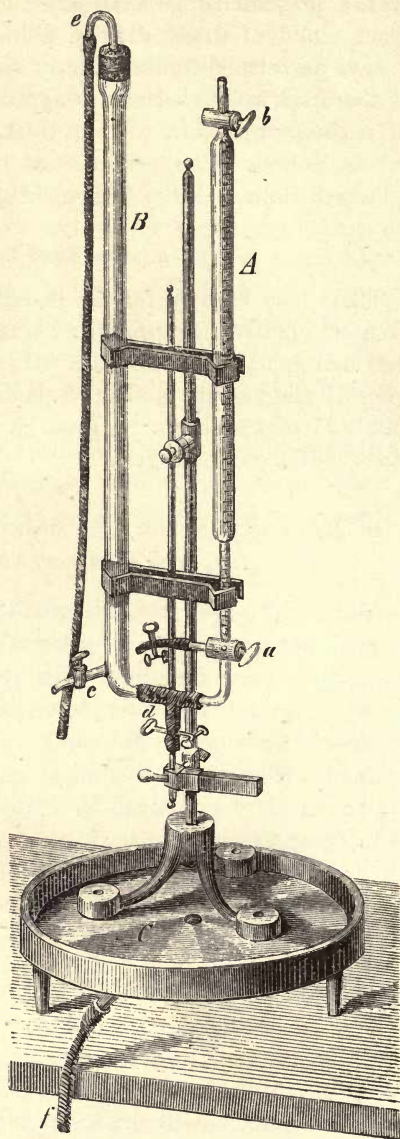
Manipulation.—Open the tap *b*, and by means of the tap *a* put the measuring-tube *A* in communication with the gas to be analyzed; by means of an india-rubber pump or an aspirator,

Fig. 43.
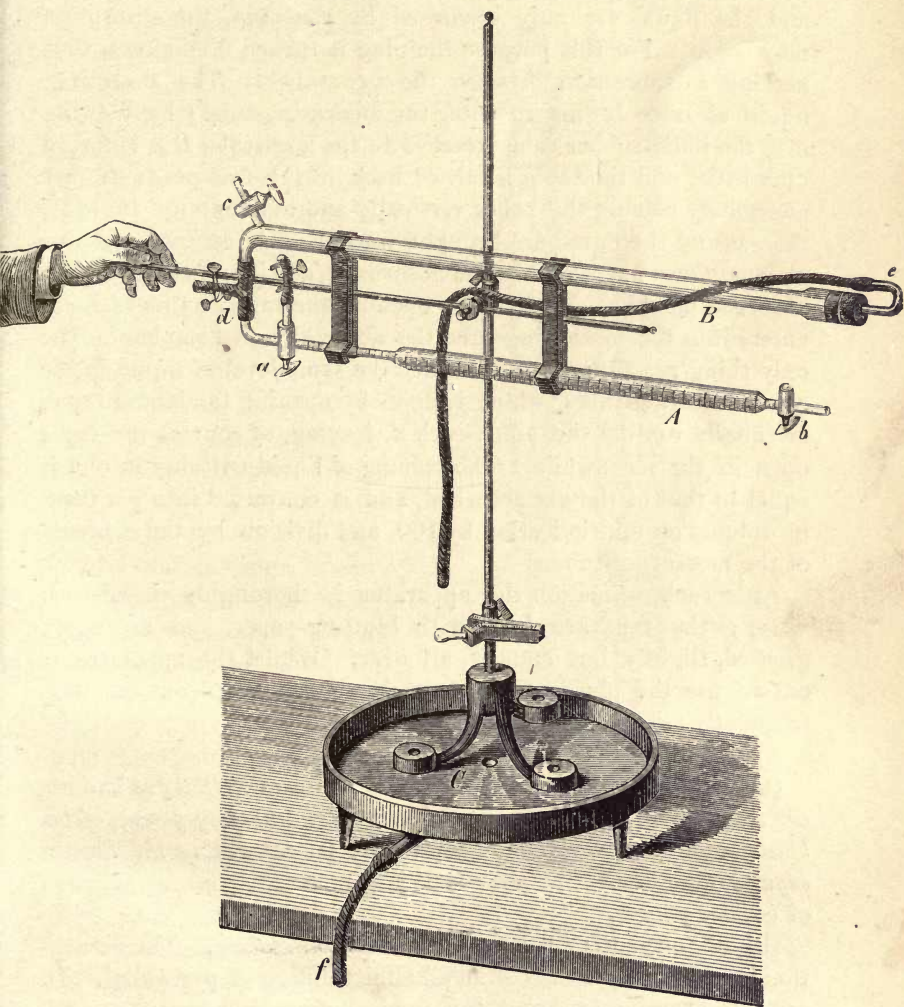
cause a current of the gas to traverse the measuring-tube till all air has been driven out. According to whether this is done by pressure or by aspiration, either the tap *a* or the tap *b* is closed first

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.

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. 43), 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 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.

(c) *For the examination of commercial liquid carbon dioxide and of natural sources of gaseous carbon dioxide.* A. Lange (Chem. Ind. 1900, p. 530) has modified Winkler's gas-burette for the above-mentioned purposes, as shown in fig. 44. Tube *A*, holding 100 c.c., is at top contracted into a tube holding 5 c.c. and divided. It is connected by means of an elastic joint with tube *B*, but there is no branch tube serving as an outlet. The elastic tube, put on the bent tube *c*, is at the bottom continued into a glass tube reaching into the 250 c.c. bottle *D*, fixed on the stand. The apparatus is charged by pouring into *B* sufficient caustic potash solution of spec. grav. 1·297 to fill *A* and *B* rather more than halfway up. Now the cork, with tube *c* and the elastic tube, is put on *B*, and by means of another elastic tube, put on *b*, air is blown into *A*, until the level of the liquid is below tap *a*, which is then closed. *B* is now filled with potash solution as well as *c* and the elastic tube. *D* is also filled with the same solution, and by opening tap *b* it is ascertained that the bore of this tap is also filled. The apparatus is now ready for use. By turning the three-way tap *a* 90 degrees, the gas can be passed into *A*.

Fig. 44.
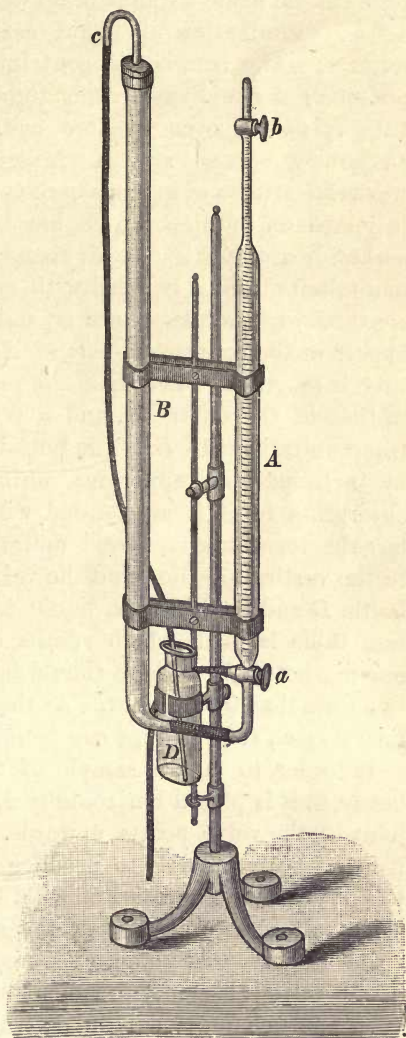
When b has been closed and a opened, the potash solution, in consequence of the absorption of CO_2, will flow from D into B and A. After the absorption has been finished and b has been opened, the solution flows back into D and the level is automatically restored in a, whereupon the apparatus is again ready for work. There is no trouble about handling the potash solution, and upwards of 400 tests can be made without renewing it.

The examination of liquid carbon dioxide is carried out as follows :—The iron bottle containing it is placed in an upright position ; a coupling-piece is tightly screwed on and an elastic tube is drawn over its free end. The valve of the bottle is cautiously opened and is regulated so as to yield a regular, moderate stream of gaseous carbon dioxide. Then the elastic tube is joined on to tap a, which has been turned so as to admit the carbon dioxide into A; the air escapes through the open tap b. After one minute tube A is filled with carbon dioxide, and this can be continued till needle-shaped crystals of potassium hydrocarbonate appear in the contracted part of A. Then b is closed, the elastic tube is taken off, whereupon the pressure within A becomes equal to that of the outer air, and a is turned 90 degrees, so that A communicates with B. The potash liquor at once rises in A, and by inclining the apparatus, ultimately to the horizontal, the absorption in A is accelerated without forming a vacuum. At last the apparatus is moved upwards and downwards, then fixed in the vertical position and the volume is read off, after lifting up bottle D and levelling the liquid in D and A. Or else a correction table is made which admits of taking the reading without moving bottle D. There should be no greater difference between two tests than 0·05 p. cent. As the contracted part of A is divided into $\frac{1}{20}$ c.c., the readings can be made to 0·01 c.c.

In order to take a sample of the liquid contents of an iron bottle, this is placed horizontally on a stool so that the coupling-joint of the valve points upwards. By slowly opening the valve it is generally possible to produce a suitable, moderate stream of CO_2, but small quantities of solid CO_2 are always ejected. With some valves the adjusting of the stream is very troublesome; it issues in jerks and sometimes stops, but with the slightest touch of the valve it becomes so violent that the elastic tubes are thrown off. In such cases a reducing-valve can be interposed, but the gas must be allowed to issue long enough to drive out all the air

from the valves : in this case the results agree completely with those obtained directly from the contents of the bottle.

Holste (Zeitsch. f. d. ges. Kohlensäure-Industrie, 1897, p. 462) has described a method for calculating the true percentage of air in the carbon dioxide from the figures obtained for the gaseous and the liquid portion.

(d) *Examination of liquid chlorine and strong chlorine gas ; estimation of carbon dioxide in electrolytic chlorine.* The process is carried on as in (c), but the absorbent is a concentrated solution of ferrous chloride, which absorbs the chlorine rapidly and in quantity, leaving air and carbon dioxide behind. In a second burette the gas is treated with caustic-potash solution, which absorbs chlorine and carbon dioxide, leaving the air alone behind. The carbon dioxide is found by difference. Probably it is best to first saturate the ferrous-chloride solution with carbon dioxide. his process is analogous to Lange's as above described, but has not yet been introduced into factories.

b. HONIGMANN'S GAS-BURETTE.

The burette *A* (fig. 45) 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. 45.

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* (fig. 46) carries a funnel *t*, provided with a mark, and is closed at the top by the three-way cock *a* (comp. p. 33) and below by the plain tap *b*, ending in an almost capillary tube. 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, about 3 millimetres wide, 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. 46.
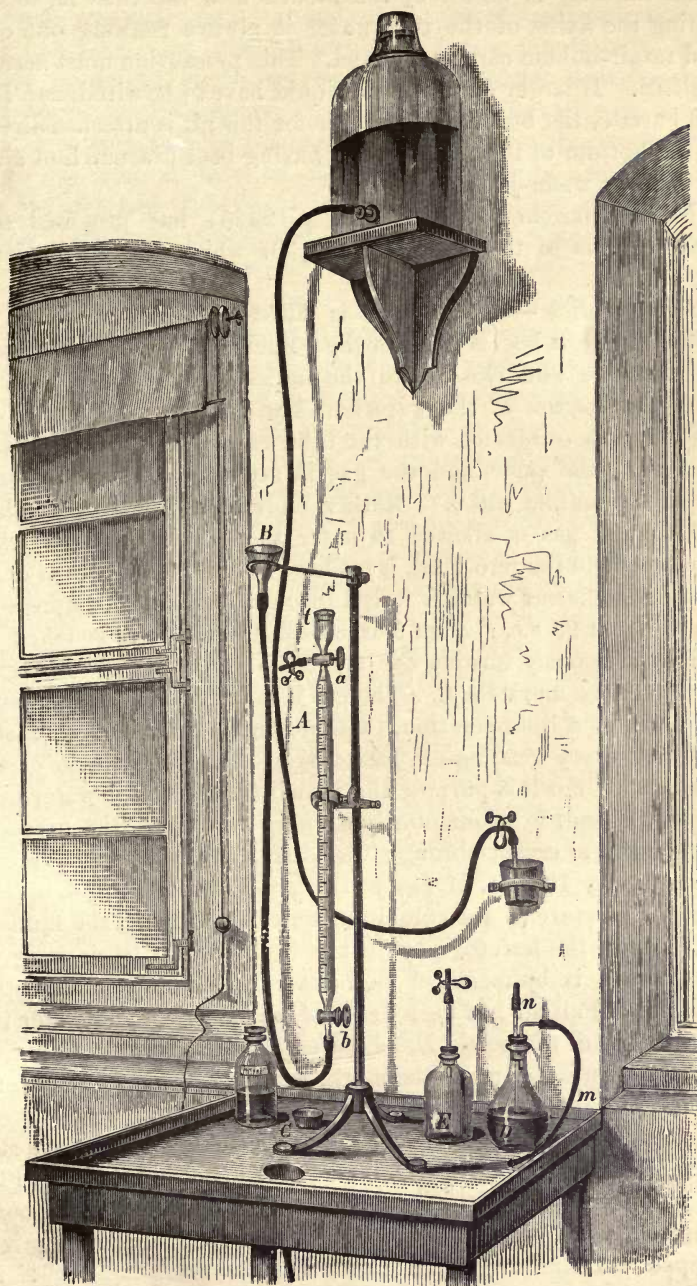
same time air is blown by the mouth into the tube m, so that during the fixing of the tube water is always running out of n, and no air-bubble can be enclosed. This precaution must *never* be omitted. If larger quantities of liquid have to be withdrawn from the burette, the bottle E may serve for this; it is attached directly to the bottom of the burette, after having been evacuated of air by means of a water-jet pump.

Bleier (Berichte, 1895, xxviii. p. 2423) has proposed some modifications of the Bunte burette, for which we must refer to the original.

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, a different 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.

But as this manipulation requires the use of a large quantity of water, by which some of the gas may be dissolved, it is best to draw off most of the absorbing-liquid by suction and wash by means of a few c.c. of water, which is again sucked off, repeating this as often as may be necessary.

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 mixtures 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.

C. *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.   The 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 M. 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. 47) contains, from the zero-mark

Fig. 47.
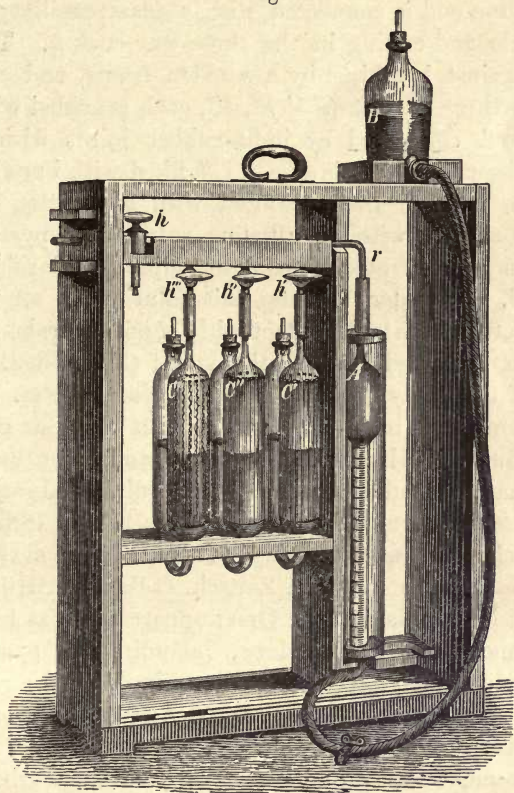
at its bottom to the upper capillary end, exactly 100 c.c., but its graduation (in $\frac{1}{5}$ c.c.) only extends to 40 c.c. and ceases where

* This apparatus is an imitation of that constructed by Schlösing and Rolland, which is not so well known; both depend upon a principle first applied by Regnault and Reiset. It has met with extraordinary approbation, and has undergone many modifications, *e. g.* by Salleron, Aron, Ferd. Fischer, Rob. Muencke, E. Tomson, Corn. Heinz, H. Petrzilka, O. Bleier, P. Fuchs, H. Fahlenkamp, and others. The author prefers the form now constructed by Rob. Muencke of Berlin, and therefore describes that only.

the tube is enlarged. In order to protect the gas contained in this burette from the influence of the changes of external temperature, 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 plainly 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 provided with a capillary tube 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.

In lieu of the easily broken glass taps Naef (Chem. Ind. 1885, p. 289) recommends india-rubber tubes with globular glass valves (so-called Bunsen valves) ; Olschewsky prefers ordinary pinchcocks. Lunge has added to the three ordinary absorbing-tubes a contrivance for burning hydrogen (Chem. Zeit. 1882, p. 262 ; comp. the chapter on hydrogen). Thörner (Chem. Zeit. 1891, p. 768) and Hankus (Oesterr. Zeitsch. f. Berg- u. Hüttenwesen, 1899, p. 81) have enlarged the Orsat apparatus so as to comprise all contrivances for combustions, including an apparatus for evolving oxyhydrogen gas, an explosion pipette, and an induction-coil. This seems going too far in the direction of complicating the apparatus.

The above-mentioned liquids serve for absorbing carbon dioxide, oxygen, and carbon monoxide respectively. The whole apparatus, as may be seen from the description, is specially intended for analyzing combustion-gases. Oxygen can also be absorbed by moist phosphorus in the shape of thin sticks; comp. p. 68. In this case the vessel C'' contains no glass tubes, but 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 it 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, the outer ends of the vessels 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*, 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.

In order to save the trouble of carrying the gas backwards and

forwards from the burette into the absorbing-tubes, Namias
(Stahl u. Eisen, 1890, p. 788) and Le Docte (Chem. Zeit. 1900,
p. 375) have constructed automatically moving contrivances.
Cario (Germ. Pat. No. 98667 ; Chem. Zeit. 1898, p. 977) describes
an automatically acting apparatus, slightly deviating from Orsat's.
L. Kaufmann & Co. (Chem. Zeit. 1901, Rep. p. 26) describe,
under the name of " Ados," an apparatus for automatically
analyzing furnace-gases and continually registering the results.

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 : ammoniacal solution of cuprous
> chloride ; comp. p. 73.

For controlling the efficiency of furnace-fires it is usually
sufficient to estimate the carbon dioxide in the chimney-gases.
The *calculation of the loss of heat by the chimney-gases* is dealt
with in Lunge's ' Taschenbuch für die Sodaindustrie' &c., 3rd ed.
p. 130, and by F. Fischer in Lunge's 'Chem. techn. Untersuchungs-
methoden,' Berlin, 1899, vol. i. p. 216.

An apparatus not exactly serving for gas-analysis, but con-
structed for an approximate estimation of the action of a
furnace-fire, is *Hempel's gas lanthorn* (Chem. Ind. 1896, p. 98),
the principle of which is the alteration in the size of a flame
corresponding with the percentage of oxygen in the gas by which
it is fed.

F. Fischer (Dingl. Journ. cclviii. p. 28) has employed the
Orsat apparatus for estimating the total acids of pyrites-kiln
gases, as well as their percentage of oxygen. For this purpose he
charges the apparatus with petroleum in lieu of water. [This
causes some inconveniences, therefore other apparatus is preferable
for the above purpose ; comp. below.—*Translator.*]

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. 48) is closed at the top by a three-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

Fig. 48.
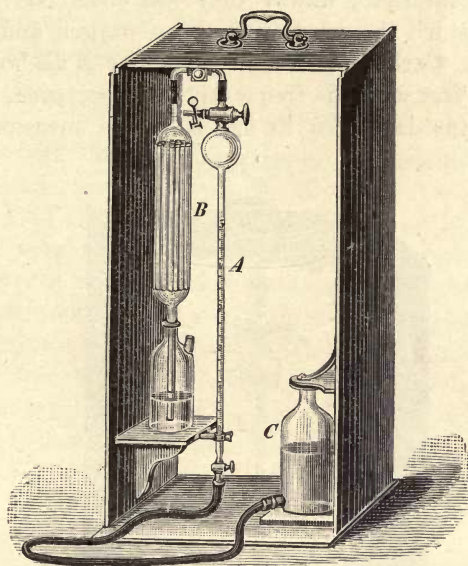
narrow cylindrical part only contains 5 c.c., and is divided into tenths of a cubic centimetre. The lower end of the burette is connected by a narrow elastic tube with the level-bottle *C*, containing pure water; from the upper part a glass capillary tube leads to the absorbing-vessel *B*, which is filled 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. 69). Carbon dioxide in particular is all but indifferent in this case, a fact which is frequently of importance.

The apparatus is shown in fig. 49. The measuring-tube *A*

Fig. 49.
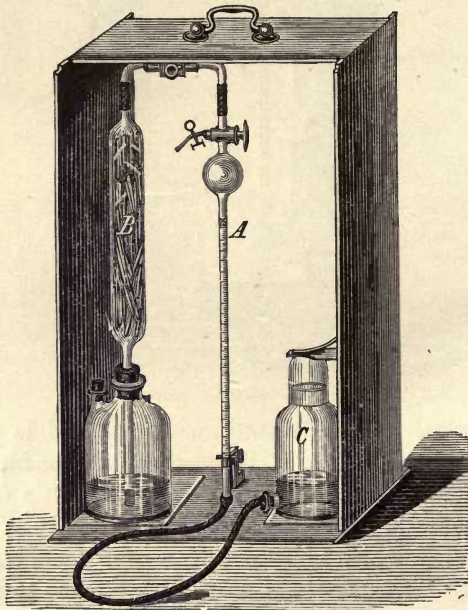
has a three-way cock at the top, but no tap at the bottom. It

* Modified by the author.

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.

Applications :—

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

Very important for absorptiometrical gas-analysis have been the improvements introduced by W. Hempel ('Ueber technische Gasanalyse,' 1877; 'Gasanalytische Methoden,' 3rd ed. 1900, p. 29). He employs "gas-pipettes" as first constructed by Ettling & Doyère, suitably modified, each serving for retaining a certain constituent of the gas, and easily attached to the gas-burette by means of a connecting capillary or removed in the same way. This secures the advantage that the measuring of a gas and its treatment with one or more absorbents can be separately performed at leisure and in a very efficient way. Consequently his methods secure a degree of accuracy otherwise unattainable in technical gas-analyses and with water as a confining liquid.

The *simple gas-burette* (fig. 50) consists of two communicating cylindrical glass tubes, 1·5 cm. wide, 65 to 68 cm. long. The measuring-tube A ends at the top in a capillary, 1 mm. wide and 3 cm. long, upon which a piece of india-rubber tube, 5 cm. long, is drawn and fixed gas-tight by means of copper wire covered with silk. This tube, as well as that required for closing the gas-pipettes, should be the best thick-walled black india-rubber tubing, 2 mm. bore and 6 mm. outer diameter. Closely above the capillary the elastic tube carries a small pinch-cock, 5 cm. long, which is taken off when not required. From this pinch-cock

arrangement down to the bottom mark, 3 or 4 cm. above the foot of the burette, the tube holds 100 c.c., divided into $\frac{1}{5}$ c.c., and showing on one side the figures 0 to 100, on the other from 100 to 0. Tube A is cemented into a base made of thin cast-iron or of

Fig. 50.
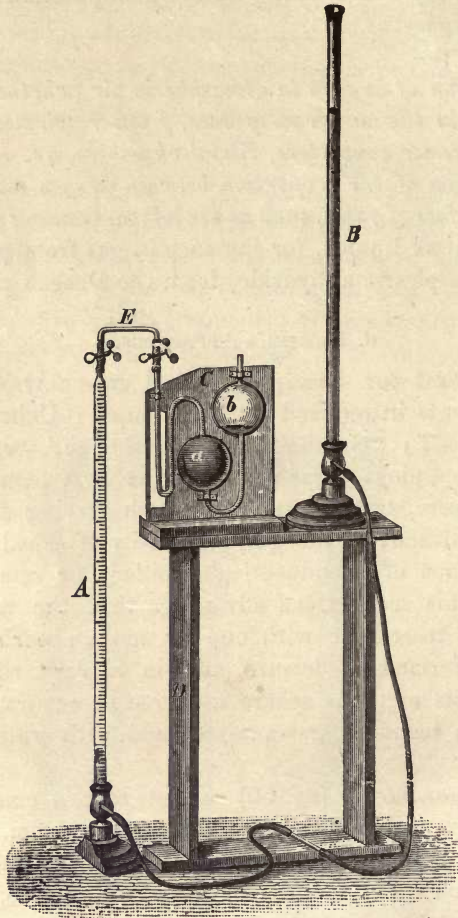
polished black wood, so that the lower contracted end is carried out sideways at a right angle through this base. The level-tube B, which is open at the top, possesses a similar base; its bottom end is connected with that of the burette A by an india-rubber tube, which is conveniently intercepted in 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.

In lieu of this simple burette, one with a water-jacket may be used, as shown in fig. 51. This jacket is 3 cm. wide, and serves for keeping the temperature of the gas constant; it possesses two branches, at top and bottom, through which, if needful, water may be run in a constant stream. The burette is fixed in the jacket

Fig. 52.

Fig. 51.
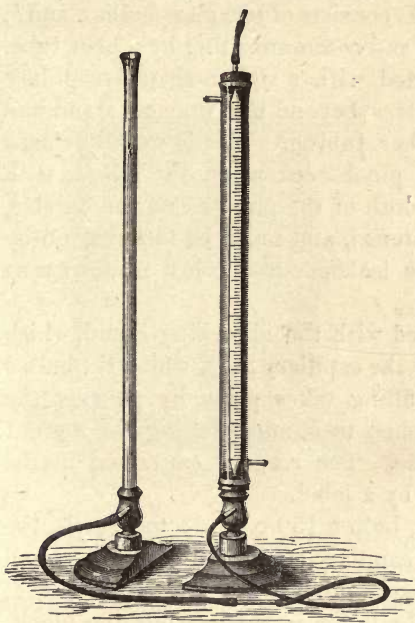
by means of india-rubber corks. In the great majority of cases there is no necessity for employing such a water-jacket.

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. 52). 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 versâ*.
Otherwise the arrangement and manipulation are the same as with
Hempel's burette.

Gas-pipettes.—The pipette shown in fig. 50 at *C* is what is called
the *simple absorption-pipette*. It consists of two glass bulbs *a* and *b*,
fixed on a wooden or iron stand and communicating by a bent tube.
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 by a pinch-cock when the pipette is in
use. The india-rubber tubes, both of the pipette and the burette,
should 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. The reagent contained in the
pipette is marked on the stand by a label.

Bulb *a* should hold 200 c.c., bulb *b* 150 c.c.; if too small, the
pipette must be rejected. The capillary connected with *a* is closed
by an elastic tube and pinch-cock during use, and when out of
use by a piece of glass rod. The latter is put in while the pinch-
cock is closed, and is removed subsequently; otherwise air
will be forced into the capillary and the thin column of liquid
will be broken. Should this happen, the capillary must be emptied
by sucking for a moment at *a*, and be filled again by blowing air in
the opposite direction. The end connected with *b* is closed by a cork
when out of use, which must be removed before using the pipette.

A pipette for *fuming oil of vitriol* (comp. p. 66) is shown in
fig. 53. Here the small bulb *d* above *a* is filled by the glass-
blower with small bits of glass, which enlarges the absorbing
surface and renders agitation unnecessary. When not in use,

the ends of this pipette are closed by small glass caps, which may be made quite tight by means of small india-rubber rings.

The simple tubulated absorption-pipette (fig. 54) is arranged in the same way as fig. 50, 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
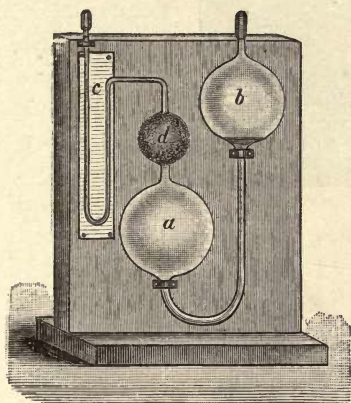
Fig. 53.　　　　　　　　　　Fig. 54.
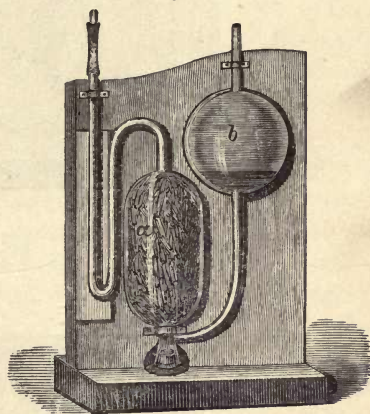
stopper a glass rod, tapering upwards, upon which is fixed a zinc cylinder perforated in the centre, the vessel *b* being filled with dilute sulphuric acid. As soon as the stopping of the capillary is removed, the acid gets to the zinc and hydrogen is given off. This is allowed to continue till all air 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. 55) is used for keeping absorbents which suffer change in contact with atmospheric air, like alkaline solution of pyrogallol, or a solution of cuprous chloride in hydrochloric acid, or those which give off irritating vapours, such

H

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

Fig. 55.

Fig. 56.

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
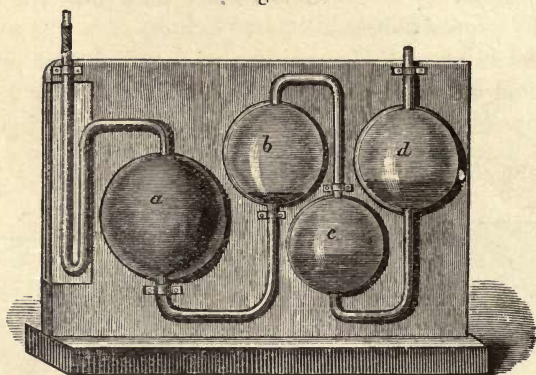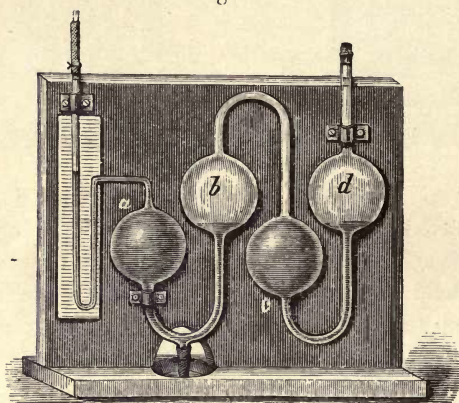through a short funnel, this can be done by attaching to the outer
end of the bulb *d* an india-rubber tube with pinch-cock, and
withdrawing the air contained in the apparatus by now and then
sucking it out.

It is very convenient to attach to the lowest point of the connecting-tube between *a* and *b* a short branch, closed by a pinch-cock or glass rod, for the purpose of charging the pipette (fig. 56). After doing so, the pinch-cock is replaced by a bit of glass rod. The stand, if made of wood, is cut out accordingly.

Exactly in the same way the *pipette for solid reagents*, fig. 54, can be combined with a second pair of bulbs forming a water-lute.

Arrangement and Manipulation of Hempel's Apparatus.

The general arrangement is shown in fig. 50, p. 94. The measuring-tube *A* and the capillary of the pipette *C*, after providing both with pinch-cocks as shown, are connected by the glass capillary *E*, made from a tube 18 cm. long, 6 mm. outside diameter, and 1 mm. bore, by bending it on each side into a right angle, with limbs 4 or 4½ cm. long, the ends being rounded off. The pipette is placed on a wooden bench, 46·5 cm. high, 37·5 cm. wide, and 10·0 cm. broad.

Manipulation.—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. 31); 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 con-
tents 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, cause the gas to 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 acetic acid, introduced into the end of the
elastic tube.

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. 52, p. 95), and
the reading is taken after waiting two minutes for the water to
flow down.   First the measuring-tube is raised with the right
hand, then the level-tube with the left, and the level of the two
liquids placed in the same plane as the eye of the manipulator.
The pipette should be previously taken off, the pinchcock is re-
moved, and the open tubes closed with their glass rod arrangements.
In the same way a second, third, &c. constituent of the gas can
be absorbed and estimated, each time employing a different
pipette.

   Applications :—

   (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 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 acidulated with sulphuric acid.

Nitric oxide . . . . with concentrated solution of ferrous sulphate, or with potassium permanganate acidulated with sulphuric acid, or with a concentrated alkaline solution of potassium sulphite (Divers, Chem. Zeit. 1898, p. 1036).

Nitrous oxide. . . . with alcohol (this is only approximate; comp. Lunge, Bericht, 1881, xiv. p. 2188).

Chlorine . . . . with solution of caustic potash, or in the presence of carbon dioxide by a solution of ferrous chloride or potassium iodide.

Hydrochloric acid . with solution of potash.

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) *Estimation of acetylene, oxygen, and non-absorbable constituents in crude acetylene*, by successive absorption :—

1st, of acetylene by fuming sulphuric acid and remeasuring in a gas-burette charged with fresh water.
2nd, of oxygen by alkaline solution of pyrogallol.
3rd, measuring the non-absorbed remainder, consisting of hydrogen, methane, and nitrogen.

(g) *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) and benzene, by fuming sulphuric acid, subsequently removing the acid vapours by employing the potash pipette.
3rd, Oxygen by alkaline pyrogallol, or copper and ammonia, or phosphorus and water.
4tn, Carbon monoxide by ammoniacal cuprous chloride in two pipettes (p. 74).
5th, Hydrogen ⎫
　　　Methane ⎬ remaining unabsorbed.
　　　Nitrogen ⎭

2. Estimation by Titration.

We have discussed this in a general way, p. 48. The composition of the *standard liquids* is indicated by a table in the Appendix.

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. 57), 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, which are conveniently made 8 or 10 cm. long.

Fig. 57.

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; for outdoor work they are carried in special bottles, as shown in fig. 58, 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. 59, 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 filling is complete, the end of the inlet-pipe is drawn out of the
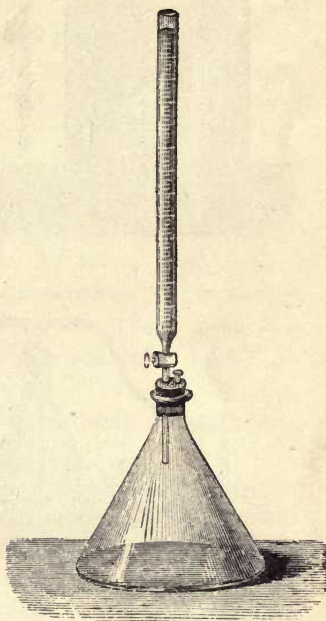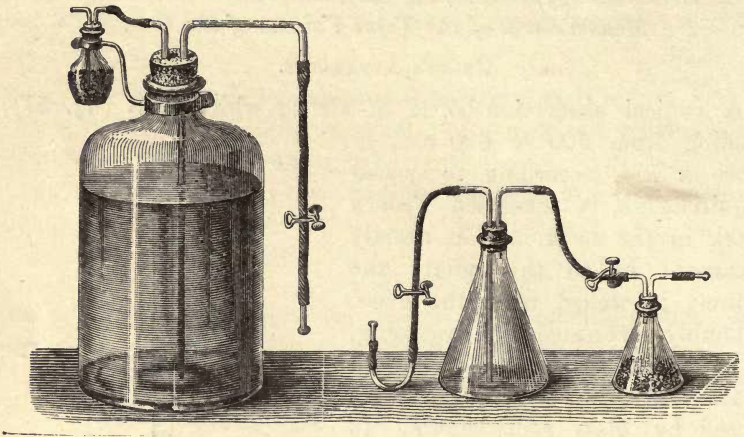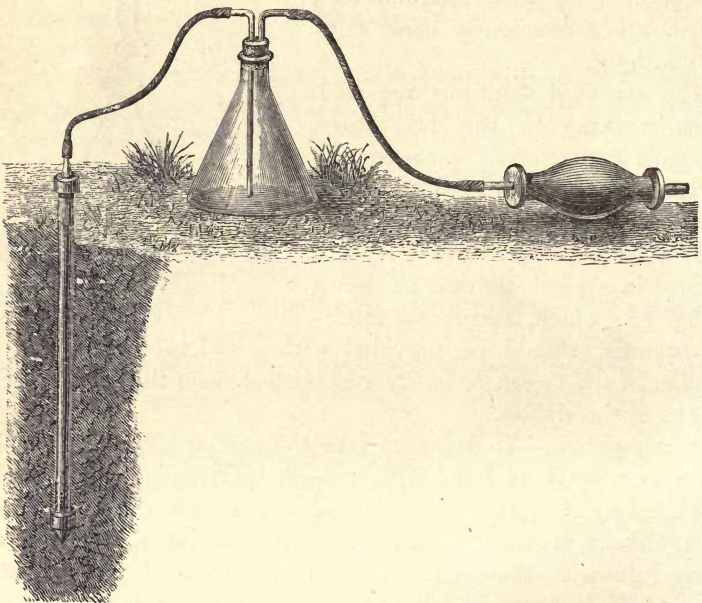
Fig. 58.

Fig. 59.

cork, the hole in the latter is quickly closed by a glass roa, 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

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 to 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.

Applications :—

1. *Estimation of carbon dioxide in atmospheric air, in the expired air, in air taken from rooms, pits, caves, walls, subsoil, tombs, in coal-gas, &c.*—Titrated baryta-water is employed for the absorption, normal oxalic acid for retitrating, and phenolphthalein 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 millims.

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 employed 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 sul-
phocyanide 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 given on p. 105)*.

   Cyanhydric acid can be estimated in a similar way.

   3. *Estimation of chlorine in the gases from chlorine-stills, from
Deacon's process, in the air of bleaching-powder chambers, &c.*—The
absorption is caused by a normal solution of arsenious acid in

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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.*

sodium bicarbonate ; the excess 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. 105).

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. 60), holding about a litre, 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, or else provided with many pin-hole outlets, and closed by the pinch-cock *q* ; the other

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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.*

side neck serves for the outlet-pipe, which is connected with the tin aspirator *B*, or a glass-bottle aspirator, like fig. 13, p. 16. Below the outlet-pipe of the latter, closed with a tap *h*, a glass jar *C* is placed, which is divided into cubic centimetres, and serves for holding and measuring to half a litre the water which runs out.


Fig. 60.

Manipulation.—Fill the absorbing-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 entirely, there is no leakage in the apparatus.

In order to test a gas, a suitable 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.

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,
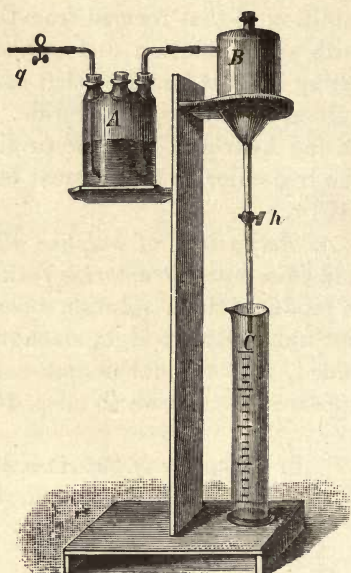
cleaning, and refilling of the vessel A need only be attended to at intervals.

The quantity of water run into the cylinder C is measured. Its volume is that of the unabsorbed residue 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 the 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. 24, or by the table contained in the Appendix, or by the help of the apparatus described on p. 26, 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 ; but in this case the bottle should be freshly charged each time, because otherwise CO_2 might be given off and cause an error by increasing the volume of the unabsorbed gas.

　　　　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 Freiburg, 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 :—

$$\frac{100 \times n}{n+m} = \frac{100 \times 25 \times 1\cdot118}{(25 \times 1\cdot118)+295} = 8\cdot74 \text{ per cent.*}$$

2. *Estimation of total acids in pyrites-kiln gases and analogous gases.*—Since these gases may contain a considerable percentage of *sulphur trioxide*, which escapes the iodometrical estimation, Lunge (Zeitsch. f. angew. Chem. 1890, p. 563) recommends expressing the value of such gases not merely by their percentage of sulphur dioxide but by that of total acids ($SO_2 + SO_3$). In such cases the best absorbent is a standard solution of potassium or sodium hydroxide, of which a suitable quantity is added to the water contained in A (fig. 60). An alcoholic solution of phenolphthalein

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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.*

(1 : 1000) serves as indicator, a few drops of which suffice to stain the liquid a vivid red. The gas is not aspirated through it continuously, but in small portions at a time, agitating each time about half a minute to secure complete absorption. Any arsenious acid present is kept out by interposing a small glass tube filled with asbestos. When the alkali is approximately neutralized the red colour turns pale; the point when the last shade of red has vanished is easily noticed even in the dusk or with artificial light when employing a white paper as background. This point marks with phenolphthalein the formation of normal sulphite and sulphate (Na_2SO_3 and Na_2SO_4) ; other indicators are not admissible, as they yield different results for sulphurous and sulphuric acid.

If HCl is present, it can be estimated in the liquid by titrating the total acids by Volhard's method with silver nitrate and re-titrating with ammonium sulphocyanide, or as described on p. 106 in the footnote.

Apart from the total acids, the percentage of SO_2 by itself can be estimated in another sample of gas, as described under No. 1, p. 109 ; that of SO_3 is found by difference.

Example. The reduction apparatus, p. 26, shows 113·2 c.c.

(a) *Estimation of sulphur dioxide.*
Each c.c. of iodine solution $= 1$ c.c. SO_2.
Employed 25 c.c. iodine solution (n).
Water flowed out (m) $= 320$ c.c. $= 282$ c.c. corrected.

$$\frac{100 \times n}{n+m} = \frac{100 \times 25}{25 + 282} = 8·23 \text{ vol. per cent. } SO_2.$$

(b) *Estimation of total acids.*
Each c.c. of caustic soda solution $= 1$ c.c. SO_2.
Employed n c.c. soda solution $= 25$ c.c.
Water flowed out (m) $= 295$ c.c. $= 261$ c.c. corrected.

$$\frac{100 \times n}{n+m} = \frac{100 \times 25}{25 + 261} = 8·74 \text{ vol. per cent. } SO_2 \text{ as } SO_2 + SO_3.$$

(c) *Estimation of sulphur trioxide.*
On subtracting the percentage found at (a) from (b), we find the quantity of SO_3 present expressed in volume per cent. SO_2 :

$$8·74 - 8·23 = 0·51 \text{ vol. per cent. } SO_2 \text{ as } SO_3.$$

Hence the sulphur in the kiln-gas is present to the extent of

94·17 per cent. in the form of SO_2.
5·83   ,,   ,,   ,, SO_3.

3. *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 sul-
phuric acid. The end of the reaction is shown by the decolori-
zation of the liquid. The absorption takes place slowly and some-
times incompletely.

Example :—

Barometer (B), 728 millims.

Temperature (t), 22°.

Titre of the potassium permanganate : 1 c.c. $= 0 \cdot 1$ c.c. N_2O_3.

Permanganate employed 2·5 c.c. ; $n = 0 \cdot 25$.

Water run out (m) $= 410$ c.c. ; or, corrected, $= 35 \cdot 61$ c.c.

Hence :—

$$\frac{100n}{n+m} = \frac{100 \times 0 \cdot 25}{0 \cdot 25 + 353 \cdot 61} = 0 \cdot 0706 \text{ per cent. by volume} *.$$

b. The Minimetrical Method.

The principle of this method was enunciated by Dr. R. Angus
Smith ; it has been improved by G. Lunge (Zur Frage der Venti-
lation, 1877) and later on by Lunge & Zeckendorff. Its original
shape is shown in fig. 61.

Fig. 61.

The conical flask *a* (fig. 61)
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 stop-
per. The tube *b* is continued into
a wider one, serving to receive

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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. 107). Moreover it is for the most part not advisable to estimate
the N_2O_3 by permanganate (comp. footnote to p. 123).—*Translator*.

a caoutchouc valve which opens only inwards. 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 a glass tube open at both ends is inserted, which is carried through the perforated cork.

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 the finger-pump is compressed, can only open outwards, 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 to refill it 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 a number 1 English red syringe, provided with a mouthpiece made of bone, such as are found at all shops selling surgical instruments. These 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 ascertain the volume of the aspirated gas, minus that retained by the absorbing-liquid.

The shape adopted later on by Lunge and Zeckendorff (Zeitsch. f. angew. Chem. 1888, p. 396) for their method as here described is shown in fig. 62. The ball B here holds 70 c.c.

Manipulation.—The tube b (fig. 61) 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 finger-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

I

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, he 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.

Fig. 62.

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.

Lunge and Zeckendorff's method is best adapted for the rapid, if only approximate, estimation of small percentages. The apparatus is compact, simple, and cheap. Its employment by the original minimetrical method of estimation (for which it was 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*
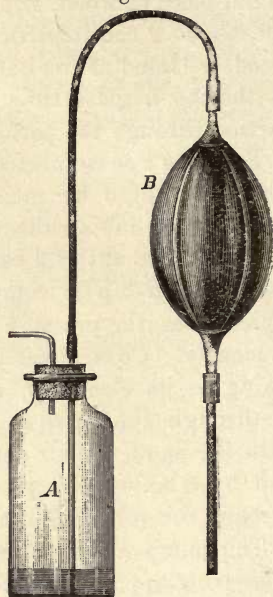
air, *in the air of rooms, coal-pits, caves, walls, subsoil, tombs, &c.,* employing titrated *baryta-water* for absorption and phenolphthalein as indicator. An alcoholic solution of the latter is added in only just sufficient proportion to produce a distinct pink colour. After each working of the finger-pump 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. $= 0.104$ c.c. carbon dioxide.

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

Baryta-water employed 25 c.c.; $n = 0.104 \times 25 = 2.60$ 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 $\dfrac{100 \times n}{n+m} = \dfrac{100 \times 2.6}{2.6 + 540} = 0.47$ per cent. by volume.

2. *Estimation of carbon dioxide in air &c., by means of sodium carbonate and phenolphthalein as indicator.*—This is the method worked out by Lunge and Zeckendorff (*loc. cit.*). It is founded on the fact that a solution of sodium carbonate, stained red by phenolphthalein, is decolorized when sodium bicarbonate has been formed. A decinormal solution of sodium carbonate, containing 5.30 grams Na_2CO_3 per litre, is stained red by 0.1 gram phenolphthalein. Before using it 2 c.c. is diluted to 100 c.c. with distilled water, freed from CO_2 by boiling. For each test 10 c.c. of this dilute solution is employed, and the air to be examined is blown through by means of the finger-pump until the pink colour changes into faint yellow. With highly contaminated air 2 to 4 charges of the finger-pump are sufficient ; pure air requires 30 to 40 charges. The percentage of CO_2 in the air cannot be calculated from the data as above, but is found by the following, empirically ascertained table * :—

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* Fuch's (Lehmann, Prakt. Hygiene, 1900, p. 149) has shown these empirically found results to be correct. But he prefers employing solutions of twice the strength, *i. e.* 4 c.c. of the first solution diluted to 100 c.c. The results agree to about $\frac{1}{10}$ of their value.—*Translator*

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

3. *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.

4. *Estimation of total acids in dilute pyrites-kiln gases, acid smoke, chimney-gases, &c.* is performed as in No. 2, p. 110.

5. *Estimation of sulphur dioxide in dilute burner-gas, chimney-gas, metal-smelting gas, &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, p. 114.

c. APPARATUS FOR ESTIMATING SINGLE CONSTITUENTS OCCURRING IN MINUTE QUANTITIES.

In these cases the gas has to be brought into contact with a suitable absorbent in the most intimate, lasting, and repeating way. Many apparatus have been constructed for this purpose, of which we quote the following :—

(1) *Winkler's Absorption-coil* (fig. 63) consists of a spiral glass tube A, resting on three glass feet, and filled with the absorbing-liquid nearly to the bulb E. Into its bottom is sealed the inlet-tube B, provided with a bulb D and a pointed end F. From the latter the gas issues in small bubbles, like a string of beads, along the coils of A, and leaves the coil only after a comparatively long time at C_1. The coil must rise gently and quite evenly ; otherwise the

small bubbles unite into large ones, which lessens the contact between the gas and the liquid. This is neglected in most of the coils found in the trade, wherefore the following suitable dimensions are given for two different sizes of coils (in millimetres) :—

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

Fig. 63.
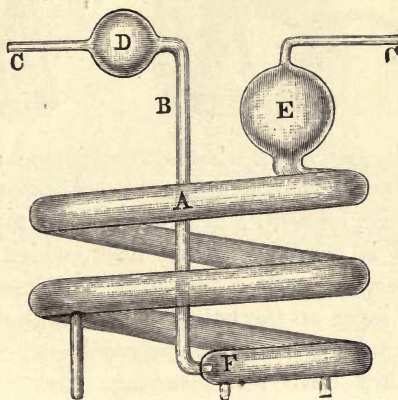
Good absorption-coils are excellent, especially for such cases where the object is less the estimation than the complete removal of a constituent, *e. g.* carbon dioxide from air. In such cases size 1 is always employed.

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

(2) The *Ten-bulb tube* seen in fig. 64 has a very good effect, and is recommended by Lunge (Zeitsch. f. angew. Chem. 1890, p. 567) in preference to most other apparatus of its kind. It is very convenient for the purpose of estimating the absorbed constituent volumetrically or gravimetrically.

(3) Very efficient also are *the absorbing-flasks* devised by Volhard (Ann. Chem. clxxvi. p. 282), and improved by Fresenius (Zeitsch.

f. analyt. Chem. 1875, p. 332) by the addition of another bulb
in the lateral tube, as shown in fig. 65. The flasks are made
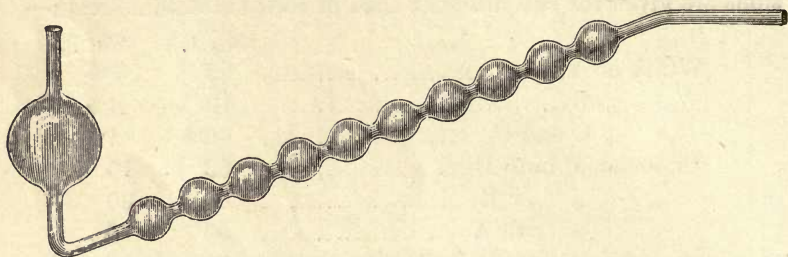
Fig. 64.

Fig. 65.

about 11 cm. high, and 7 cm. wide at the bottom; the mouth,
2·5 cm. wide, is either closed by a simple perforated india-rubber
cork with glass tube, or with a ground-in glass stopper. About
25 to 50 c.c. liquid is poured into the flask, which liquid under
the pressure of the gas partly enters into the lateral tube, partly
remains in a thin layer at the bottom. The absorption is still
more certain when two or three of these receivers
are employed. They have the advantage that
after finishing the absorption the liquid can be
titrated in the same flask, and cannot be forced
back by atmospheric pressure (no more than in
the ten-bulb apparatus, fig. 64).

Fig. 66.

(4) *Drehschmidt's Absorbing-cylinder*, fig. 66.—
The central tube, fixed in the india-rubber cork,
carries at the bottom a closed glass bulb, with
pin-holes in the upper part, by which the gas is
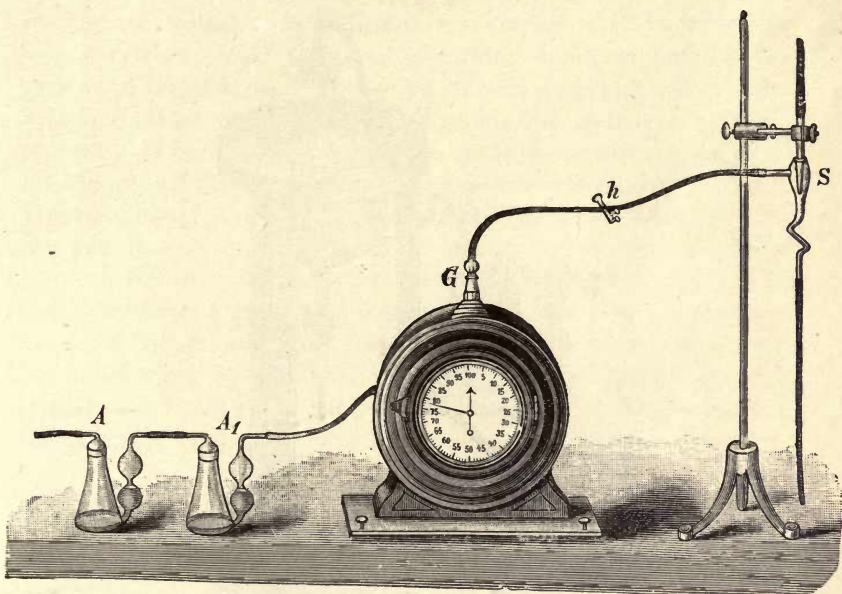thoroughly divided.

General Arrangement.—The gas is aspirated by
means of air-pump S (fig. 67); it passes first
through the flasks A and A_1, filled with the ab-
sorbing-liquid, or in their place through a ten-bulb tube, and
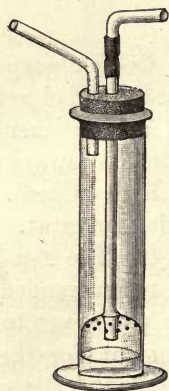
then into the gas-meter, G, where the non-absorbed gas is mea-
sured.   Pinch-cock *h* serves for regulating the flow of gas so

Fig. 67.

that the suction is only just sufficient to carry the gas through
the absorbing-liquid.

In lieu of the air-pump and gas-meter an *aspirator* (*d*, fig. 68)
can be employed, and the water run out from it during the
experiment can be measured or weighed.   This must be done
especially in such cases where a gas-meter would be acted upon
by acid gases or stopped up by tarry matters.   Crude coal-gas,
for instance, is first passed, by tap *a*, through bottle *b*, where
ammonia &c. is retained by water; *c* serves for retaining hydrogen
sulphide, tar, &c., for which purpose the enlarged outlet pipe is
filled with cotton-wool.   The aspirator *d* is best made to hold a
certain volume, say 20 litres; its upper tap may be provided with
a micrometer-screw for regulating the flow of water, but this
can be efficiently performed by means of a screw pinch-cock placed
on the connecting-tube.

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

Fig. 68.
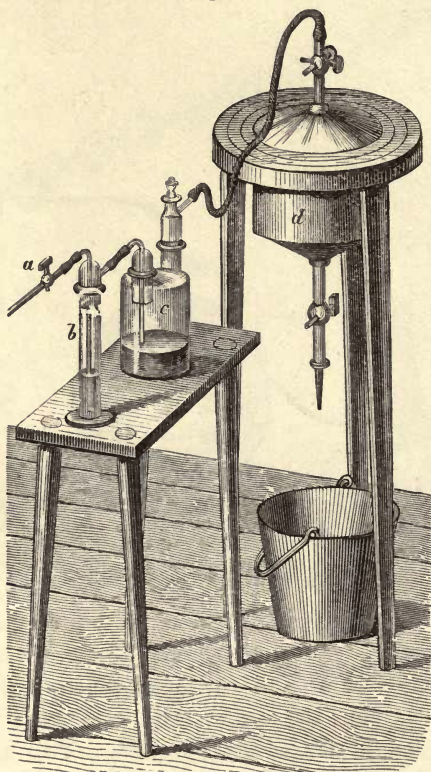
volume of standard solution saturated, shows the volume of the absorbable gaseous constituent $= n$, while that which is not absorbed, m, is expressed by the quantity of water run out of the aspirator. For exact measurements the latter must be reduced to the standard pressure and temperature; otherwise 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 10 to 50 litres per hour or 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 methyl-orange or hematoxylene. The measured absorbing-liquid is put in the cylinder *b* (fig. 68), 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. 47) 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 ; with Drehschmidt's absorbers (p. 118) even 60 or 70 litres per hour is allowable.

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 :

$$\frac{100n}{n+m} = \frac{100 \times 2 \cdot 62}{2 \cdot 62 + 100,000} = 0 \cdot 00262 \text{ per cent. by volume.}$$

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 cyanogen and hydrogen cyanide in coal-gas.*—
Drehschmidt (Journ. f. Gasbeleucht. 1892, pp. 221,268) has utilized
the fact that cyanogen * and hydrocyanic acid, even in the pre-
sence of carbon dioxide and hydrogen sulphide, are retained by
solution of caustic potash, containing freshly precipitated ferrous
hydrate, with formation of ferrocyanide, for the estimation of
both. For each test he employs 100 litres of gas and passes it with
a velocity of 60 or 80 litres per hour through two absorbing-
cylinders with bulb ends (fig. 66, p. 118) : the first charged with
15 c.c. of a solution of ferrous sulphate (1 : 10) and 15 c.c. caustic-
potash solution (1 : 3) ; the second 5 c.c. ferrous-sulphate solution,
5 c.c. caustic-potash solution and 20 c.c. water. The caustic-
potash solution is made from pure commercial caustic potash, free
from chloride, 1 part in 3 water; this solution has a specific
gravity of 178 and contains 20 per cent. KOH. An approximately
equivalent sulphuric acid is obtained by diluting pure concen-
trated sulphuric acid with four times its weight of water. The
relation of both liquids towards each other is fixed by titration.

After finishing the absorption, mix the contents of both re-
ceivers, dilute to 250 c.c., and filter though a dry filter. 200 c.c.
of the clear filtrate=80 litres gas=16 c.c. potash solution is
neutralized with the above-mentioned sulphuric acid; add 2 grams
ammonium sulphate, 15 grams mercuric oxide (this is much more
than necessary), and a few drops ammonia, heat to boiling and
continue this gently for a quarter of an hour. After cooling
dilute to 300 c.c. and filter again through a dry filter. Of the
last filtrate pour 250 c.c.=66·66 litres gas into a 300 c.c. flask,
add 6 or 8 c.c. liquor ammoniæ spec. grav. 0·91 and 7 grams zinc
dust, shake well up, add 2 c.c. caustic-potash solution (1 : 3), fill
up to the mark, shake up again, and filter through a double filter.
Titrate 200 c.c. of the filtrate=44·44 litres gas by adding 10 c.c.
decinormal silver solution, acidulating with nitric acid, and re-
measuring the excess of silver by decinormal ammonium sulpho-
cyanide and iron-alum as indicator. 1 c.c. decinormal silver
nitrate=0·002584 grams cyanogen.

Freiberg municipal gas, thus examined, required for 44·44 litres
gas 1·44 c.c.=0·003721 grams cyanogen, and hence contained 8·37
grams cyanogen in 100 cubic metres.

* Comp. on the detection of free cyanogen in coal-gas, Kunz-Krause, Zeitschr.
f. angew. Chem. 1901, p. 652.

3. *Estimation of nitrogen trioxide in vitriol-chamber gases &c.*—
The absorbent is concentrated sulphuric acid, 25 c.c. of which is
placed in each of the two Volhard-Fresenius flasks (fig. 65, p. 118)
employed; 10 litres or more of gas is slowly drawn through by
means of an aspirator with a pressure-gauge attached to it,
measuring the outflowing water. The liquids of both flasks are
mixed and the N_2O_3 absorbed estimated by one or other of the
following methods :—

(*a*) Part of the acid is placed in a glass-tap burette and is slowly
run into a measured volume of standard potassium permanganate
solution, strongly diluted with water of $40°$, agitating all the time,
until the colour has been discharged. The reaction is :

$$5\, N_2O_3 + 4\, KMnO_4 + 6\, H_2SO_4 = 10\, HNO_3 + 2\, K_2SO_4 + 4\, MnSO_4 + H_2O.$$
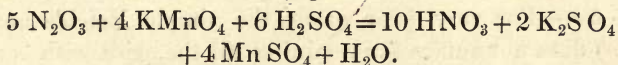
From the volume of acid required and that of the standard
permanganate employed, we calculate the number of c.c. perman-
ganate (n) which would have been decolorized by the whole 50 c.c.
acid, m being represented by the volume of water run out of the
aspirator.

(*b*) A measured volume of acid is run into a known volume of
permanganate solution, and the excess of the latter retitrated by
hydrogen peroxide.

(*c*) Or else the nitrogen is estimated gas-volumetrically by the
nitrometer method, p. 33, thus converting it into nitric oxide,
1 c.c. of which is $0·0016993$ grams N_2O_3.*

4. *Estimation of chlorine* takes place by absorption in a solution
of arsenious acid in sodium carbonate and retitration with iodine
solution and starch.

5. *Estimation of hydrogen chloride in roasting-gases, chimney-
gases, saltcake furnace-gases, exit-gases of hydrochloric-acid con-
densers, &c.,* by absorption in standard alkaline solution and re-
titration with standard acid. If other acids are present, the HCl

* It is well known that nitrogen trioxide is almost entirely dissociated into
nitric oxide and peroxide when in the state of vapour. By the above described
methods we learn how much of the equivalent mixture of $NO+NO_2$ is present
in the gas. But as in most cases the chamber-gases do not contain precisely
such a mixture, but an excess of either NO or NO_2, the processes quoted in the
text under (*a*) and (*b*) are *not* to be recommended, as they would give quite a
wrong idea of the real state of the chambers. The process (*c*), *i. e.* the esti-
mation of total nitrogen acids by means of the nitrometer, is the only one which
should be employed.—*Translator.*

may be titrated in the same liquid by means of silver nitrate and ammonium sulphocyanide (p. 106) *.

If chlorine is present together with hydrogen chloride, the gas is passed through a solution of arsenious acid in sodium bicarbonate. In one part of the liquid the chlorine is estimated by retitration with iodine, in another the total HCl as in No. 6 †. Since 1 vol. chlorine furnishes 2 vols. HCl, the total volume of HCl found must be diminished by twice the volume of free chlorine, to find the HCl originally present.

6. *Estimation of total acids in poor gases from the manufacture of sulphuric and hydrochloric acid, sulphite cellulose, ultramarine, glass, superphosphate, from roasting-furnaces, hop-driers, brick-works, &c.*—For very poor gases the simple Reich's apparatus (p. 107) does not suffice for retaining all the acids with certainty. It is preferable to use a ten-bulb tube (p. 118), charged with a known volume of standard alkali and connected with a 10 or 15 litre water-aspirator. The gas is slowly drawn through the liquid, which is then washed into a beaker and retitrated with standard acid and methylorange. 1 c.cm. of decinormal soda-solution (4·000 grams NaOH per litre) shows 0·0040 gr. SO_3, 0·0049 H_2SO_4, 0·0032 SO_2, 0·00365 HCl, 0·0020 HF, &c. The result is expressed in *grams total acid per cubic metre of the gas,* taken at 0° C. and 760 mm. pressure ‡. The " total acids " are reduced to one special compound—*e. g.*, in the manufacture of sulphuric acid they are expressed in terms of SO_3, although comprising SO_2, SO_3, H_2SO_4, and the acids of nitrogen; in the manufacture of saltcake and hydrochloric acid in terms of HCl. In Prussia and Saxony (comp. Chemische Industrie, 1898, p. 535) the total acidity of gases from the manufacture of sulphuric acid or sulphur trioxide is limited to a maximum of 5 grams SO_3 per cubic metre, except in factories working with blende, where the utmost limit is 8 grams, always taking the sample *before* the gases enter the chimney. In Great Britain the limit is 4 grains SO_3

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* Or by silver nitrate and potassium chromate in the neutralized liquids (see footnote to p. 106).—*Translator.*

† In this case no addition of potassium chromate is necessary for titrating the neutralized liquid with silver nitrate, as the sodium arseniate is quite as good an indicator.—*Translator.*

‡ In Great Britain it is expressed in *grains per cubic foot.* 1 grain per cubic foot = 2·287 grams per cubic metre ; 1 gram per cubic metre = 0·4372 grain per cubic foot.—*Translator.*

per cubic foot at 60° F. and 29 inches pressure $= 9.15\ SO_3$ grammes per cubic metre at 15°·5 C. and 760 mm. pressure.

Example :—

Estimation of total acidity of the exit-gases of the manufacture of sulphuric anhydride.

Employed decinormal sodium hydrate solution
    (diluted in ten-bulb tube to 125 c.c.) . .   50·00 c.c.
Employed in retitration : decinormal acid . .   38·05 „
Neutralized by total acids . . . .   11·95 „
    $= 11.95 \times 0.0040 = 0.0478$ gram SO_3.

Water run out of the aspirator, 11·320 litres.
Gas-reduction apparatus shows 111·3 c.c.

Hence corrected volume of gas employed $= 10.170$ litres.

1 cub. met. of gas contains total acids (SO_2, SO_3, and H_2SO_4, in terms of SO_3) :

$$\frac{0.04780 \times 1000}{10.170} = 4.70 \text{ grams.}$$

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-apparatus are the same as described on p. 116 *et seq.*, and the calculation of the results is generally made in the same way as is there indicated.

Applications :—

1. *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. 65, p. 118), each of them containing 25 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 through two Volhard's apparatus, each containing 20 c.c. of ammoniacal silver solution. For greater security three absorbing-vessels may be employed before and behind

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* See the preparation of this later on (p. 140).

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 first two receivers on the one hand, and those of the last two receivers on the other, 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 the usual manner. From the weight of this precipitate that of the *acetylene* may be deduced by means of the formula (founded on the research by E. H. Keiser, Amer. Chemical Journ. xiv. p. 285):—

$$C_2Ag_2 + 2HCl = 2AgCl + C_2H_2.$$
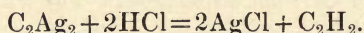
1 gram AgCl corresponds to 0·0907 gram acetylene = 78·12 c.c. in the normal state.

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 gram of silver corresponds to 0·1486 gram S, or 0·1579 gram H_2S, or 103·78 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 0·1486 gr. S, or 0·1764 gr. CS_2, or 52·12 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 grams 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*. This is generally done by burning a known volume of the gas, receiving the products of combustion in a solution of potassium carbonate containing a little bromine, and precipitating the sulphuric acid formed by barium chloride 1 gr. $BaSO_4 = 0·1373$ gr. S. Drehschmidt (Chem. Zeit. 1887, p. 1382) and F. Fischer (Zeitsch. f. angew. Chem. 1897, p. 302) describe special apparatus for this purpose. Since 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 assumed as 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. = 24·92 c.c. acetylene.

Ag a = 0·0111 gr. = 1·15 ,, hydrogen sulphide.

Ag b = 0·3888 gr. = 20·26 ,, carbon disulphide.

Total sulphur :—

Silver a = 0·0111 gr. = 0·001647 gr. S.

,, b = 0·3888 ,, = 0·057765 ,,

100 cubic metres of gas contain 62·68 grams sulphur *.

Expressed in per cent. by volume :—

Acetylene . . . . . 0·02620 p. c.

Hydrogen sulphide 0·00121 ,,

Carbon disulphide 0·02126 ,,

* 1 gram per cubic metre = 0·4372 grains per cubic foot.--*Translator*.

2. *Estimation of sulphuretted and phosphoretted hydrogen in crude acetylene.*—The sulphur in acetylene-gas exists mostly in the shape of organic sulphur compounds, which have been separated from it by Knorre and Arndt (Verh. Gewerbfleiss, 1900, p. 155). It is, however, admissible to express them in terms of H_2S or in grams S per cubic metre. Rossel & Landriset (Zeitsch. f. angew. Chem. 1901, p. 77) found in acetylene varying quantities of sulphur, dependent both upon the quality of the calcium carbide and the process employed for evolving the acetylene. They found per 100 cub. metres from 21 to 111 grams $S = 0.01466 - 0.07746$ vol. per cent. of H_2S; and in 100 cub. metres a maximum of 73 grams phosphorus.

Lunge & Cedercrentz (Zeitsch. f. angew. Chem. 1897, p. 651) have indicated the following process for estimating both impurities at the same time :—A known volume of the gas is slowly passed through a ten-bulb tube (p. 118), charged with 2 or 3 per cent. solution of sodium hypochlorite. The liquid is washed into a graduated flask, and in one half of it the sulphuric acid is gravimetrically estimated as barium sulphate (1 gr. $BaSO_4 = 0.1373$ gr. $S = 0.1459$ gr. $H_2S = 95.86$ c.c. H_2S), in the other half the phosphoric acid as magnesium pyrophosphate (1 gr. $Mg_2P_2O_7 = 0.2784$ gr. $P = 0.3055$ $H_3P = 200.91$ c.c. H_3P).

3. *Detection and approximate estimation of very small quantities of sulphur dioxide and sulphuric acid in air, suspected of being contaminated with acid smoke.*—Ost (Chem. Zeit. 1896, p. 170) and H. Wislicenus (Zeitsch. f. angew. Chem. 1901, p. 689) chemically fix the acid contained in the suspected air of forests &c. by exposing to it for a long time wooden frames, of a superficial area of one square metre, covered with loose cotton tissue, impregnated with barium carbonate by moistening with baryta-water. This gives an idea of the quality of *soot* present, and later on, by incineration and estimation of the sulphate contained in the ash, the quantity of *sulphur acids* present in the air. For the conclusions to be drawn from this process (which is not yet fully worked out) we must refer to the original.

III. Estimation of Gases by Combustion.

1. General Remarks on the Combustion of Gases

Those constituents of a gaseous mixture which cannot be estimated by absorption, owing to the want of a suitable reagent, are, if possible, transformed by *combustion with oxygen* into compounds capable of being condensed or absorbed. Hereby both the combustible gas and the oxygen are removed, causing a *contraction of volume* from which the volume of the combustible gas can be deduced, as the combustion always takes place in definite proportions of volumes.

A further contraction of volume, which stands in definite proportion to the volume of the gas burned and thereby admits of estimating the latter, is produced by absorbing any carbon dioxide formed during the combustion.

The *oxygen* required for this purpose is only exceptionally employed in the pure state in technical gas-analysis, mostly in the shape of *air*, and of course always in moderate excess.

Only three gases need be considered which cannot be estimated absorptiometrically :—

Hydrogen, to be burned by oxygen to liquid water.

Methane, to be burned by oxygen to liquid water and gaseous, but absorbable, carbon dioxide.

Nitrogen (plus *Argon,* &c.), not combustible, remaining at the end of the analysis as gaseous and directly measurable residue.

The hydrogen, both free and as a constituent of methane, yields *liquid* water, because the gas to be analyzed is previously saturated with moisture.

Suppose we have, as described p. 102, successively removed by absorption *carbon dioxide* (by caustic potash), *heavy hydrocarbons* (by fuming sulphuric acid), *oxygen* (by alkaline pyrogallol, &c.), and *carbon monoxide* (by ammoniacal cuprous chloride), we find a *non-absorbable remainder of gases* which we measure. We then transfer it to a Hempel's or Bunte's burette, and employ it entirely or partially for the estimation of hydrogen, methane, and nitrogen, or some of these gases. First we must add a known volume of oxygen or air, enough to suffice for the combustion. In order to ascertain this, we assume the gaseous remainder to *consist entirely of combustible gas,* neglecting the nitrogen, and taking the oxygen in air roughly $=20$ per cent. by volume.

K

Hydrogen, when burning, acts thus : $H_2 + O = H_2O$; hence 3 vols. gas (2 vols. H + 1 vol. O) = 0 vol. liquid water.

The contraction, K, is = 3 vols., and of these 2 vols. had been previously present as hydrogen; therefore

$$H = \frac{2K}{3} \text{ vols.}$$

If the gas to be burned is sure to contain no methane, we must add to each 2 vols. of it 1 vol. oxygen or 5 vols. air, *i. e.* for each c.c. of gas 2·5 c.c. air.

Methane gives the following reaction :

$$CH_4 + 4O = CO_2 + 2H_2O.$$
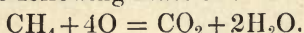
Hence 2 vols. $CH_4 + 4$ vols. O = 6 vols. gas furnish on combustion 2 vols. $CO_2 + 0$ vol. liquid water.

The contraction K, occurring on combustion, is :

$$K = 6 - 2 = 4 \text{ vols.}; \text{ hence } CH_4 = \frac{K}{2} \text{ vols.}$$

If the carbon dioxide, whose volume is equal to that of the methane burned, is afterwards removed by absorption in caustic potash, the above 6 vols. gas (2 vols. $CH_4 + 4$ vols. O) vanish altogether, and the *total contraction* K_1 is = 6 vols. or $CH_4 = \frac{K_1}{3}$ vols.

Hence to each 2 vols. of a gaseous remainder containing methane we must add before combustion (without troubling about any hydrogen or nitrogen present) 4 vols. oxygen or 20 vols. air; but this is a minimum quantity, which is best somewhat exceeded.

Besides hydrogen and methane it would be possible to estimate *other combustible gases* by this method, applying the contractions shown in Table 5 of the Appendix. But these gases are more suitably estimated absorptiometrically, as far as this is possible; combustion is at most only applied to the detection of small quantities, which cannot be directly measured by weighing or titrating the products of combustion.

Just as hydrogen can be burned by oxygen and thus determined, *vice versa* the percentage of *oxygen* in a gaseous mixture can be ascertained by mixing it with a measured excess of hydrogen, effecting the combustion, and calculating the oxygen from the contraction.

2. Methods of Combustion.

A. *Combustion by Explosion.*

The inflammation of an explosible gaseous mixture, suitably confined, by the electric spark, for the purpose of estimating one or the other of the gases taking part in the explosion by means of the subsequent contraction, is the oldest of all combustion methods for gases. It was applied by Volta to *eudiometry* : *i. e.*, the deflagration of a measured volume of air with a measured excess of hydrogen in a measuring-tube luted by mercury (the *eudiometer*), and ascertaining the contraction which takes place. This method has since been generally introduced into the exact analysis of gases, and has been greatly improved by Bunsen (Gassmetrische Methoden, 2nd edition, 1877) and by Hempel (Gasanalytische Methoden, 3rd edition, 1890, p. 114). It now serves both for the estimation of hydrogen and of methane.

The explosion method is undoubtedly attractive by its neat character, but it is not free from drawbacks. Not every gaseous mixture can be straightway brought to explosion ; it is sometimes necessary to add electrolytic oxyhydrogen gas, or, in the presence of oxygen in excess, pure hydrogen. Nor can the simultaneous combustion of a little nitrogen be always avoided ; according to Armand Gautier (Chem. Zeit. 1900, p. 586) this collateral reaction is not constant, but varies with the other conditions. Moreover, the explosion method requires mercury as a confining liquid, as well as a somewhat bulky apparatus of galvanic battery, oxyhydrogen generator, and induction-coil, which does not make it appear very convenient for *technical* analysis in a general way. Seger's eudiometer with water-seal and india-rubber taps (Thonindustrie-Zeitung, 1878, nos. 25 & 26) has never become popular ; and Hempel, who had formerly tried to make the explosion method more suitable for technical analysis by employing an explosion-pipette, provided with electrodes for the evolution of oxyhydrogen gas and charged with caustic-potash solution (Neue Methoden zur Analyse der Gase, 1880, p. 156), has abandoned this himself. There is no better prospect for the combination of the explosion arrangement with an Orsat's apparatus, proposed by Thörner (Chem. Zeit. 1891, p. 763).

Many of the difficulties cited have been removed by Hempel's new *explosion-pipette charged with mercury*, as shown in fig. 69.

It consists of two strong tubulated glass bulbs, *a* and *b*, mounted on stands and at the bottom connected by an elastic tube covered with canvas. The *explosion-bulb a* is contracted at the top, like an ordinary gas-pipette, into a siphon-like capillary, closed by a pinch-cock or glass rod, and at the bottom carries a glass tap *h* which is connected with the *level-bulb b* by the aforesaid elastic tube. At *c* two thin platinum wires are sealed into the contracted part of the bulb *a*, which wires are 2 millimetres distant from

Fig. 69.
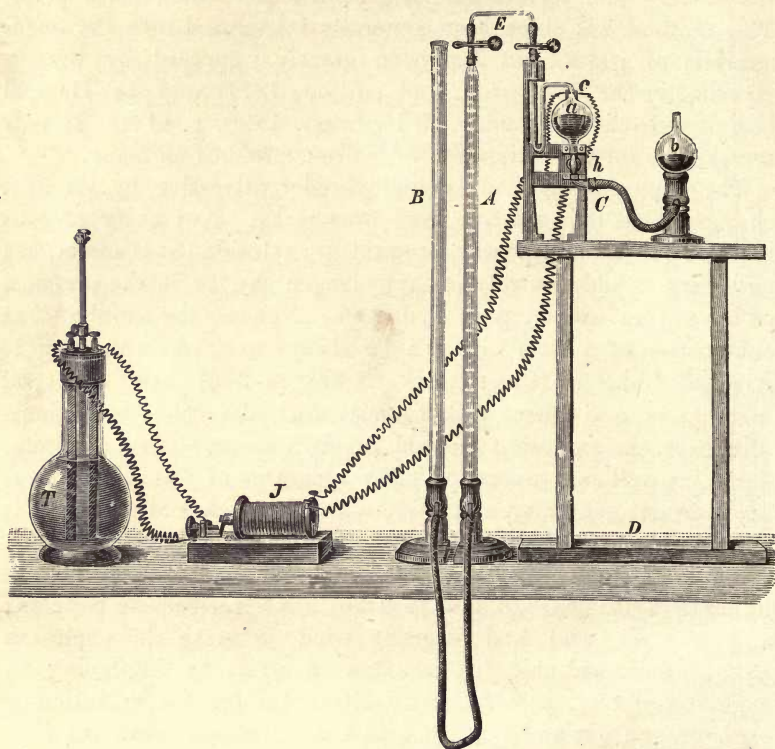
each other, so that an induction-spark can pass between them. For this purpose, the outer ends of these platinum wires are turned into loops and are connected by silk-covered copper spirals with the induction-apparatus *J*, which receives its current from the dipping-battery *T* or any other source of electricity. Both bulbs of the pipette are rather more than half filled with mercury; if

b is lifted, tap h being open, a is filled with mercury up to the capillary, and is kept in this state by closing tap h.

Manipulation.—A suitable volume of the gas to be burned is roughly measured off in the measuring-tube A of a Hempel's burette ; the level-tube B is placed on the floor, the water in the burette is allowed two minutes to flow down, and the exact reading is now taken. Tube B is again lowered and the pinch-cock of A is opened until the water has descended nearly to the bottom mark and a corresponding quantity of air has entered into the burette. After waiting again for two minutes, the second reading is taken and the volume of the gaseous mixture thus ascertained. Since 2 vols. *hydrogen* required 5 vols. air, 100 c.c. of the mixture should not contain more than $\frac{100 \times 2}{7} = 28 \cdot 57$ c.c. of combustible gas, but of course this utmost limit should never be attempted, and only about 25 c.c. of combustible gas should be employed in the case of hydrogen.

In the case of *methane*, 2 vols. require 20 vols. air; hence 100 vols. in the burette ought not to contain more than $\frac{100 \times 2}{22} = 9 \cdot 09$ c.c. of combustible gas.

If the gaseous remainder to be analyzed contains too much nitrogen to explode in a mixture with air, a sufficient amount of pure hydrogen must be added. This is best kept in stock in a Hempel's *simple hydrogen-pipette*, fig. 70. It is like an absorption-pipette for solid reagents (pp. 54, 97), into the bottom neck of which, a, a perforated zinc cylinder e has been introduced by means of a central glass rod passing through the cork. Bulb b contains dilute sulphuric acid. After all air has been expelled from the apparatus, the capillary is opened, whereupon hydrogen issues from it and is carried over into the gas-burette in the well-

Fig. 70.

known way. If the capillary is closed again, the hydrogen
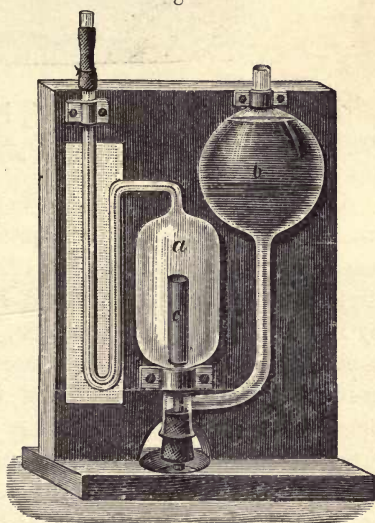
expended is renewed and forces the acid out from the cylinder into bulb *b*.

Hempel has also constructed a *composite hydrogen-pipette,* fig. 71. Two bulbs, *a* and a_1, are connected; *a* is filled with pure zinc, mixed with cuttings of platinum foil, and is closed by an indiarubber-covered glass rod put into the bottom neck *e*. *b* contains dilute sulphuric acid (1 : 10), introduced through the capillary by means of a long funnel-tube, during which process bulbs *b* and *c* are filled with hydrogen. At last a little mercury is poured into *d*, but for ordinary purposes this can be replaced by water.

Fig. 71.
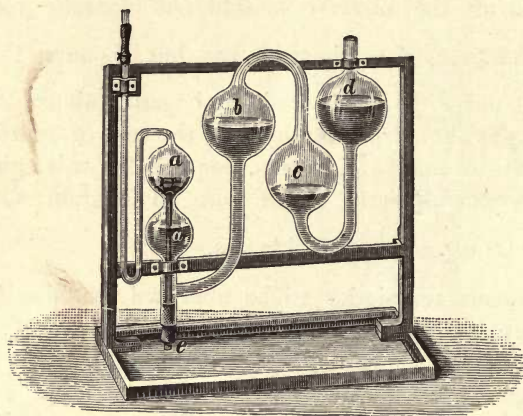
The gas given off in these pipettes is never absolutely pure hydrogen; it contains a slight amount of air, but this does not affect its use.

As soon as the mixture of the combustible gas with air, and in case of need also with a measured quantity of hydrogen, has been made, the explosion can be effected. The explosion-pipette *C* (fig. 69) is placed on a stand *D*, bulb *a* is filled with mercury by lifting *b*, and tap *h* is closed. The capillary of the pipette is connected by means of the capillary *E* with tube *A* of the gas-burette, tap *h* is opened, and by lifting the level-tube *B*, the pinch-cocks being opened, the gaseous mixture is transferred into the explosion-bulb *a*, whereupon the taps are again closed. Before closing tap *h*, it is best to lower bulb *b* and thus to produce a partial vacuum in *a*; but if the volume of gas in *a* is not large and it is not highly explosive, tap *h* may even be left

open. Now the battery T is put in motion, the current is closed. and at once the explosion occurs with a flash, the mercury being agitated and covered with a film. The gas is then re-transferred from bulb a into the burette A, and after the water has run down the contraction is ascertained.

Applications:—

1. *Estimation of hydrogen in the absence of other gases.*—In order to learn the manipulation of the method, 20 or 25 c.c. hydrogen from the hydrogen-pipette is transferred into a gas-burette, air is admitted nearly up to 100 c.c., both readings being accurately made, the mixture is transferred into the explosion-pipette, the current is closed, the gas re-transferred into the burette and the contraction read off.

Example :—

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

Found :—

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

2. *Estimation of hydrogen in the presence of other gases, but in the absence of methane,* e. g. *in non-carburetted water-gas.*—Carbon dioxide and monoxide are successively removed and estimated (p. 102), a portion of the gaseous remainder is mixed with at least $2\frac{1}{2}$ times its volume of air, the mixture having been measured is introduced into the explosion-pipette, and the experiment finished as above.

Example : *Examination of water-gas.*

Volume employed		99·8 c.c.	
After treatment by potash	95·7 c.c.		
Contraction	4·1 ,,	=4·12 p. c. CO_2.	
After two treatments by ammo-niacal cuprous chloride	} 56·0 ,,		
Contraction ... 95·7−56·0=39·7 ,,		=39·78 p. c. CO.	

Estimation of hydrogen.—Since the gaseous remainder $=39.7$ is too large to admit of adding a sufficient quantity of air, only a portion of it is employed, viz. 24·2 c.c., corresponding to 43·13 c.c. of the original gas.

Gas employed .... 24·2 c.c.
Gas + air .... 98·3 ,,
Air alone .... 74·1 ,,
Containing oxygen .... 14·8 ,,
   ,,   nitrogen .... 59·3 ,,
Volume of gas after explosion .... 65·9 ,,
   Contraction .... $98.3-65.9=32.4$,,
Corresponds to *hydrogen* (of the gas)... 21·6 ,, $=50.08$ p. c.
   ,,   ,, oxygen (from air) ...... 10·8 ,,
   ,,   ,, non-combustible gas... 65·9 ,,

Estimation of nitrogen.—The nitrogen contained in the gas is found by the difference between the volume of non-absorbed gas and the volume of hydrogen found by combustion.

Non-absorbed gas ($=43.13$ c.c. of the original gas) ... 24·2 c.c.
Hydrogen contained therein .... 21·6 ,,
Remainder .... 2·6 ,,
       $=6.02$ per cent. nitrogen.

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

3. *Estimation of hydrogen and methane occurring together,* e. g. *in coal-gas, producer-gas, coke-oven gas,* &c.—The absorbable gases are successively removed and estimated as shown on p. 102, 8 to 15 c.c. of the remainder (according to whether there is more methane or more hydrogen present) is transferred into a Hempel's burette and measured, air is added nearly up to 100 c.c. and measured again, the mixture is transferred into the explosion-pipette and after explosion the contraction is ascertained. Now the gas is treated in the caustic-potash pipette and the contraction,

caused by the removal of the CO_2, is ascertained. The latter allows of calculating the methane; by doubling the volume of the latter we learn the contraction caused by the combustion of methane, and by deducting this from the total contraction we find the contraction caused by the hydrogen, which we multiply by $\frac{2}{3}$, in order to find the hydrogen.

A check test should be made to see whether sufficient air had been employed for combustion, by transferring the last remainder of gas to a phosphorus or pygrogallol pipette, which ought always to show that an excess of oxygen has been present.

Example : *Analysis of coal-gas.*

Gas employed		99·7 c.c.
After treatment by potash......	95·9 c.c.	
Contraction	3·8 ,,	= 3·81 per cent. carbon
After treatment by fuming sulphuric acid and removal of the acid vapours by potash .	91·2 ,,	dioxide.
Contraction	4·7 ,,	= 4·71 per cent. heavy
After treatment by alkaline pyrogallol	90·6 ,,	hydrocarbons.
Contraction	0·6 ,,	= 0·60 per cent. oxygen.
After treatment by ammoniacal cuprous chloride	80·7 ,,	
Contraction	9·9 ,,	= 9·93 per cent. carbon
Non-absorbed gas	80·7 ,,	monoxide.

Estimation of hydrogen and methane.

Non-absorbable gas employed ($= 15·07$ of original gas)	12·2 c.c.	
Gas *plus* air	99·0 c.c.	
Hence air alone	86·8 ,,	
Containing oxygen	17·4 ,,	
,, nitrogen	69·4 ,,	
Volume after explosion............	79·0 ,,	
Total contraction $99·0 - 79·0$ ...	20·0 ,,	
After treatment with potash......	74·4 ,,	
Contraction (CO_2).................	4·6 ,,	$= 4·6$ c.c. CH_4.

Contraction caused by combus-
tion of methane 4.6×2 ....   9·2 c.c.   = 4·6 c.c. CH_4.
$$= 30·52 \text{ per cent.}$$
methane.

Contraction caused by combus-
tion of hydrogen $20.0 - 9.2$ ...   10·8 ,, $= \dfrac{10·8 \times 2}{3} = 7·2$ c.c.
$$= 47·78 \text{ per cent.}$$
hydrogen.

Estimation of nitrogen.

Unabsorbed gas employed ($=$
15·07 c.c. of original gas, as
before) ....   12·2 c.c.

Containing methane ... 4·6 c.c.
     ,,   hydrogen ... 7·2 ,,
               ———
               11·8 ,,
     leaving a remainder of ...   0·4 ,,   = 2·65 per cent.
nitrogen.

Results :—

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

                100·00

4. *Estimation of methane in the absence of hydrogen,* e. g. *in
fire-damp.*—To the mixture of methane and air a measured volume
of pure hydrogen must be added from a hydrogen-pipette; if
there is too little oxygen present, more air (measured) is added,
the whole is transferred to the explosion-pipette and the current
closed. After this the gas is carried back into the gas-burette,
measured, and the carbon dioxide formed (whose volume is equal
to that of the original methane) is estimated by means of the
caustic-potash pipette. This is safer than calculating the methane
from the contraction after explosion, as the hydrogen from the
pipette is never pure.

Example :—

Gas employed	85·1 c.c.
Gas + hydrogen	95·4 ,,
Hydrogen alone	10·3 ,,
Gas after explosion	70·5 ,,
After absorption by caustic potash	65·7 ,,
Contraction ($= CO_2$)	4·8 .,

Found:—4·8 c c. $= 5·63$ per cent. methane.

B. *Combustion by means of gently-heated Palladium.*

Several metals of the platinum group, as platinum, iridium, and especially palladium, have the property of causing the combustion of various gases by oxygen at a temperature below the point of inflammation. This property is exhibited to the greatest extent, the finer the state of division and consequently the greater the surface offered by those metals to the gases. Especially easy and complete is the combustion of hydrogen, if mixed with a sufficient quantity of air and carried over gently heated, finely divided palladium. Under the same conditions carbon monoxide, ethylene, and benzene are burned with a little more difficulty, but without giving any trouble. Methane, however, whose temperature of inflammation is very high (about 790°), remains unchanged at moderately low temperatures. From this follows the possibility of estimating the more easily burning gases in the presence of methane, on the principle of *fractional combustion*; and this is especially practicable for estimating *hydrogen in the presence of methane,* which two gases form the combustible remainder from the absorptiometrical analysis of gaseous mixtures.

The first to apply fractional combustion was W. Henry (Annals of Philosophy, xxv. 428), who employed *spongy platinum* heated to 177° C. Bunte (Berl. Berichte, 1878, xi. 1123) employed moderately heated *palladium wire*; Hempel (ibid. xii. 1006) *superficially oxidized palladium sponge* at a temperature of 100° C. The latter subsequently (Gasanal. Methoden, 1900, p. 159) proposed to utilize the property of finely divided palladium to retain hydrogen by occlusion, for retaining that gas without any addition of air. The author himself a long time ago proposed *palladium-asbestos* as an agent for fractional combustion, and up to this day he prefers that method as worked out by himself in the following manner.

The 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 gram 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 gram 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. palladium. 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, 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 6 millim. outside diameter, cut in pieces 16 or 18 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. 72) 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

Fig. 72.
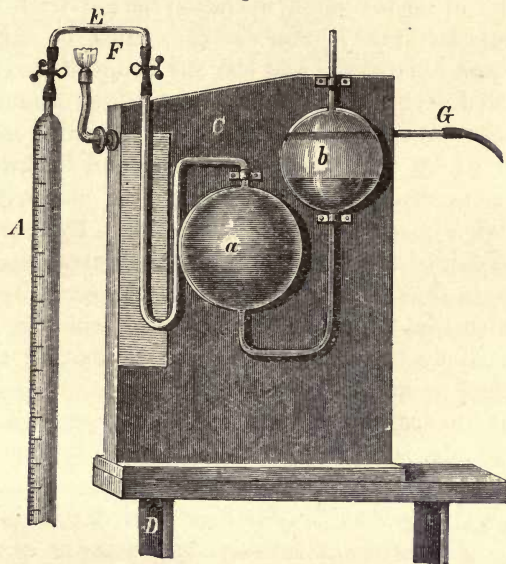
be heated at will; if the heating is to be interrupted, the flame need not be put out, but the tube *b* need only be moved a little backwards.

Manipulation.—The volume of the combustible gas contained in the burette *A* is read off; it should in no case exceed 25 c.c.

* Of course this gas-jet may be conveniently replaced by the small spirit-lamp attached to Lunge-Orsat's apparatus, fig. 73, p. 147.—*Translator*.

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 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 elevated, the pinch-cocks are opened, and the gaseous mixture is conveyed in a low 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. 133) 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. 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 .... $=22\cdot8$ c.c.
Hydrogen + air .... $=98\cdot0$ „
Hence air alone .... $=75\cdot2$ „
Oxygen contained in the same ... $=16\cdot3$ „
Oxygen required by theory ...... $=11\cdot4$ „
Excess of oxygen employed ...... $= 4\cdot9$ „
Volume of gas after combustion . $=64\cdot0$ „
Contraction .... $=34\cdot0$ „

Found :—

$$\frac{34 \times 2}{3} = 22\cdot66 \text{ c.c. hydrogen.}$$

2. *Estimation of hydrogen in the presence of other gases*, for instance *in water-gas, producer-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. 102) ; 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, $97\cdot7$ c.c.

A. *Estimation of the absorbable gases.*
After absorption by potash $87\cdot5$ c.c.
Decrease of volume . . . $12\cdot0$ „ $=12\cdot8$ volume p.c. CO_2.

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

Decrease of volume ...... 17·1 „ = 17·46 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 „

Non-combustible residue... 80·5 „

C. *Estimation of nitrogen.*

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

Non-combustible 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

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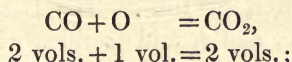
hence the volume of the air to be added must be at least $2\frac{1}{2}$ times that of the carbon monoxide present. The contraction taking place after the combustion must be multiplied by 2; but it is more accurate to absorb the CO_2 produced by combustion in the potash-pipette, and to multiply the total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

Of course the gas should be free from organic dust and tarry matters, which would equally furnish carbon dioxide on combustion. If such impurities are present, the gas should be filtered through cotton-wool and washed with concentrated caustic-potash solution ; but even then a qualitative test for carbon monoxide should be made first, as prescribed p. 74.

LUNGE'S MODIFICATION OF THE ORSAT APPARATUS [*].

Fig. 73 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 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 according to Winkler's description (p. 140). 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.)

Fig. 73.
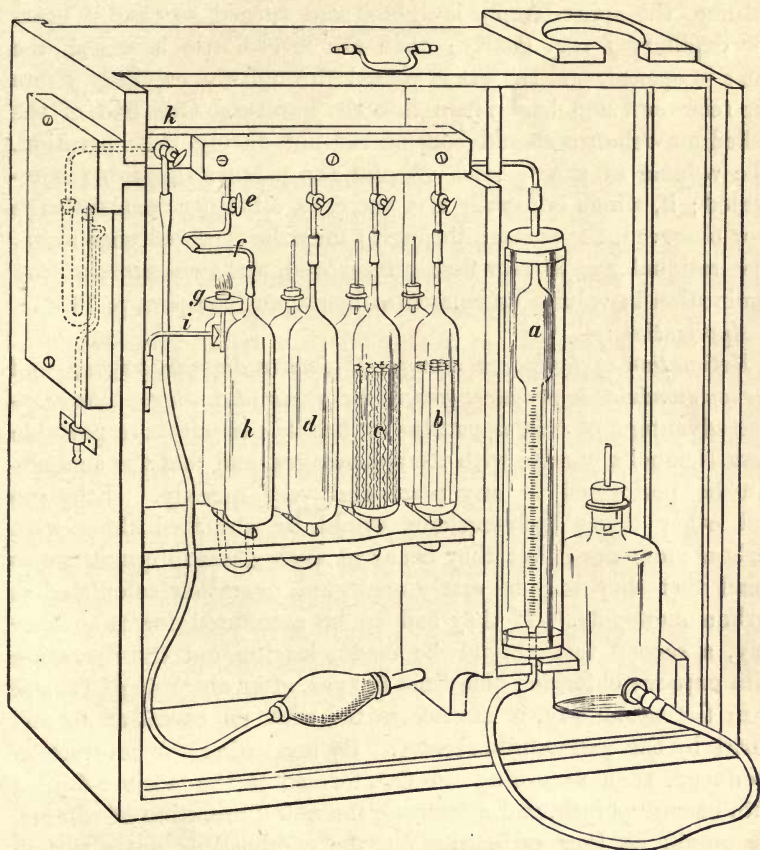
Manipulation.—After absorbing carbon dioxide, oxygen, and carbon monoxide in the manner described p. 89 (any ethylene present would be absorbed along with the carbon monoxide by the acid solution of cuprous chloride), air is admitted through the three-way cock *k* to the gaseous residue contained in 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. 143).

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 :—

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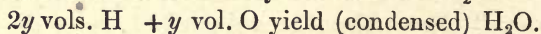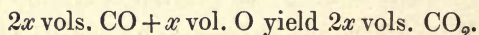
Hence :—

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

It follows from this that

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

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

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. 67) and estimated in this way.

It is unnecessary to say that any methane present will be left in the unconsumed remainder of gas; it may be estimated by any of the methods described below.

C. *Combustion by means of red-hot Platinum.*

While palladium, both in the compact state and, even better, when finely divided, causes the combustion of hydrogen, carbon monoxide, and heavy hydrocarbons, mixed with air, *at a gentle heat,* without drawing methane into the action, methane itself is burned easily and without explosion if mixed with sufficient air and brought into contact with palladium at a *bright red heat.* But as palladium has not much tenacity at high temperatures, and especially thin palladium wires easily break when getting too hot, and as in this case the principal function of the metal is a transmission of heat, it is preferable to employ *platinum,* which is hardly less active and much more durable.

a. COQUILLION'S GRISOUMETER.

Coquillion showed (Compt. rend. 1877, clxxxiv. p. 458) that a mixture of methane and air in contact with red-hot platinum or palladium burns perfectly without explosion. He utilized that observation for the examination of fire-damp ("*grisou*") by means of an instrument called a *Grisoumeter*, which is shown in fig. 74. *A* is a measuring-tube, ending at the top in a T-piece with two taps. It contains from these to the zero-point 25 c.c., the bottom part

Fig. 74.
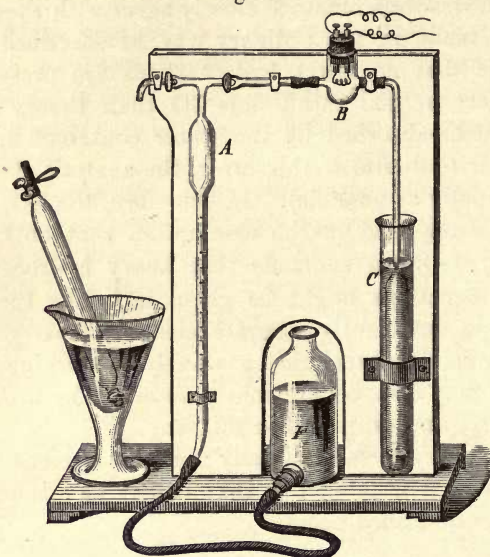
being divided. The lower end is connected with the level-bottle *F*, filled with water, and is thereby charged and emptied like Orsat's apparatus (p. 87). Through its two taps the burette can be connected either with the reservoir containing the sample of gas, or with the combustion-vessel *B*, which is hydraulically sealed by *C*. If, after combustion, the carbon dioxide is to be removed from the gas and measured, the apparatus is provided with an absorption-vessel *D* (fig. 75), charged with caustic-potash solution, and is then called a *Carburometer*. The thimble-shaped glass vessel *B* is closed by an india-rubber cork, pierced by two strong brass pins provided with screw-clamps, and connected inside the vessel by a spiral of thin platinum or palladium wire,

which can be made red-hot by passing an electric current through it.

Manipulation.—*A* is filled with water by raising *F*, connection is made with the cylinder containing the sample of gas, the latter is opened under water by removing its cork, and by lowering *F* the gas is transferred into *A*, where it is drawn in up to the zero-mark in the well-known manner. Now the current is closed and the gas is passed over the red-hot platinum spiral in *B* by means of

Fig. 75.
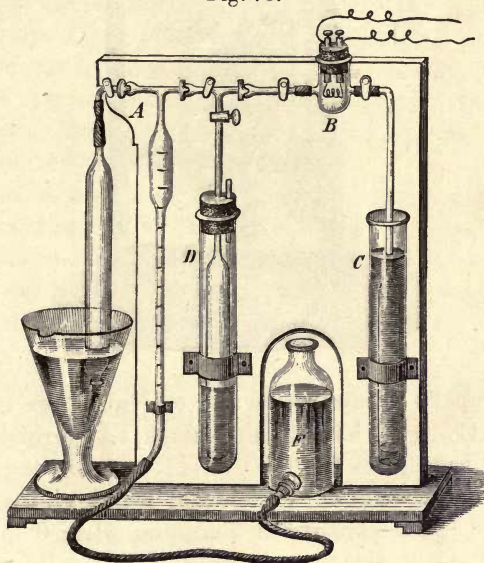
raising the level-bottle *F*, repeating this several times. After cooling the contraction is noted, half of which corresponds to the methane present. If there is too little oxygen present, more air (measured) must be admitted first.

The combustion is easy and rapid, but the cooling takes a long time and the results are only approximate. Small percentages of methane in the air of coal-pits, whose control is very important, cannot be estimated by the grisoumeter.

b. Cl. Winkler's Apparatus.

Several chemists have applied Coquillion's principle with more suitable apparatus, as Mertens (Zeitsch. f. analyt. Chem. **1887**

p. 42), Thörner (ibid. 1889, p. 642), Jeller (Zeitsch. f. angew. Chem. 1896, p. 692), and the author (Zeitsch. f. analyt. Chem. 1889, p. 286). The latter's apparatus is shown in fig. 76.

Fig. 76.
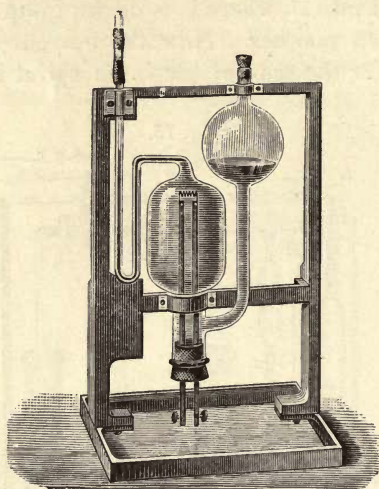
In a Hempel's tubulated gas-pipette two brass electrodes are introduced, 175 mm. long, 5 mm. thick, *not* varnished. At the bottom they have holes for the current-wires, at the top incisions in which the two ends of a platinum spiral are fixed by small screws. The spiral consists of platinum wire, 0·35 mm. thick, made by coiling it six times over a steel needle 1·3 mm. thick and leaving 1 cm. at the ends for being fixed in the above-named incision. Previously the two electrodes are coupled by a twice-perforated cork (not shown in the figure) which reaches halfway up and prevents them from moving. The electrodes ought to be 2 or 2·5 cm. distant from the top of the pipette. The pipette is then completely filled with water and is kept closed in the usual manner.

Dennis & Hopkins (Zeitsch. f. anorgan. Chem. 1899, xix. p. 179) fill the pipette with mercury, with slightly modified electrodes.

Manipulation.—The gaseous remainder, freed from absorbable constituents and hydrogen, and containing only methane and

nitrogen, is measured in a Hempel's pipette and mixed with a measured excess of air.

The burette is by means of an ordinary glass capillary connected with the pipette and the current closed. The level-tube of the burette is lifted up with the left hand, one of the pinch-cocks is opened entirely, the other one partly with the right hand, and thus the gas is *slowly* transferred to the pipette. As soon as the water has sunk below the spiral, this becomes red-hot. Now the entrance of the gas must be interrupted for a moment and the remainder of the gas introduced very gradually, in which case the combustion always takes place quietly and without any danger. If, however, the gas is passed in very quickly, or if it is first put into the pipette and the current closed subsequently, an explosion may occur which throws out the cork containing the electrodes and the water out of the side bulb.

The thickness of the wire and the number of coils (*i. e.* its length) must correspond to the strength of the current. The above given dimensions refer to a current from two small Grove elements. If the wire is too thin, it fuses; if it is too thick, it does not get hot enough, but it is not difficult to hit the proper medium.

The combustion is finished within one minute. The current is shut off, the pipette (the upper part of which gets rather hot) is allowed to cool down, the gas is re-transferred into the burette, the carbon dioxide is removed by means of a caustic-potash pipette and the total contraction noted. By dividing the latter by 3 the volume of the methane is found.

Application :—

Estimation of methane in natural gas, in " blowers " of coal-pits, in marsh-gas, coal-gas, producer-gas, &c.—Remove by absorption successively carbon dioxide, heavy hydrocarbons, oxygen, carbon monoxide (p. 102), then hydrogen by combustion with air and palladium-asbestos (p. 135), and burn the methane as described above.

In natural gas, ethane, propane, and other hydrocarbons of the series $C_n H_{2n+2}$ frequently occur in very small quantities. These are burned at the same time as methane, but with different contractions.

EXAMPLE : *Examination of natural gas.*

Employed 99·8 c.c.

A. *Absorbable constituents.*

After treatment with potash...	99·6 c.c.	
Contraction	0·2 „	= 0·20 per cent. carbon dioxide.
After treatment with fuming sulphuric acid and taking away the acid vapours by potash...........................	99·3 „	
Contraction	0·3 „	= 0·30 per cent. heavy hydrocarbons.
After treatment with alkaline pyrogallol	98·8 „	
Contraction	0·5 „	= 0·50 per cent. oxygen·
After two treatments with ammoniacal cuprous chloride	98·8 „	
Contraction	0·0 „	= 0·00 per cent. carbon monoxide.

B. *Hydrogen.*—Since natural gas contains very little hydrogen, the latter does not require much air for burning by means of palladium-asbestos, and hence most of the non-absorbable remainder can be employed for this estimation.

Employed unabsorbed gas $\dfrac{99·8 \times 78·2}{98·8}$

= 78·99 c.c of original gas ...	78·2 c.c.	
After addition of air.................	99·2 „	
Air alone	21·0 „	
Containing oxygen	4·2 „	
„ nitrogen	16·8 „	
After burning with palladium asbestos	96·5 „	
Contraction 99·2 − 96·5......	= 2·7 „	

Corresponding to :—

Hydrogen in the gas.................	1·8 „	= 2·28 per cent. hydrogen.
Oxygen from air	0·9 „	
Gaseous remainder	96·5 „	

C. *Estimation of methane.*—The gaseous remainder is considered to be pure methane; no more than 9 c.c. of it, with ten times its volume of air, is burned by means of electrically glowing platinum. By dividing the contraction thus produced by 2, the percentage of methane is found; but it is more correct to remove the carbon dioxide by caustic potash and divide the total contraction by 3 (p. 138).

Gas employed after treatment as under A and B: $\dfrac{78.99 \times 8.8}{96.5}$

$= 7.20$ c.c. of the original volume.	8.8	c.c.
After addition of air	99.2	,,
Air alone	90.4	,,
Containing oxygen	18.1	,,
,, nitrogen	72.3	,,
After combustion	85.6	,,
Contraction $99.2 - 85.6$	13.6	,,
After treatment with potash.........	78.8	,,
Contraction	6.8	,,
Total contraction $99.2 - 78.8$.	20.4	,,

Methane in gas $= \dfrac{20.4}{3}$ .... 6.8 ,, $= 94.44$ per cent. methane.

Oxygen from air .... 13.6 ,,

D. *Nitrogen* is found by difference.

Final results :—

Carbon dioxide	0.20	per cent. by volume.	
Heavy hydrocarbons	0.30	,,	,,
Oxygen	0.50	,,	,,
Hydrogen	2.28	,,	,,
Methane......................	94.44	,,	,,
Nitrogen......................	2.28	,,	,,

100.00

It is frequently assumed that the prevention of danger from
fire-damp in coal-pits need only extend to ascertaining whether
the atmosphere of the pit contains enough methane to make it

Fig. 77.
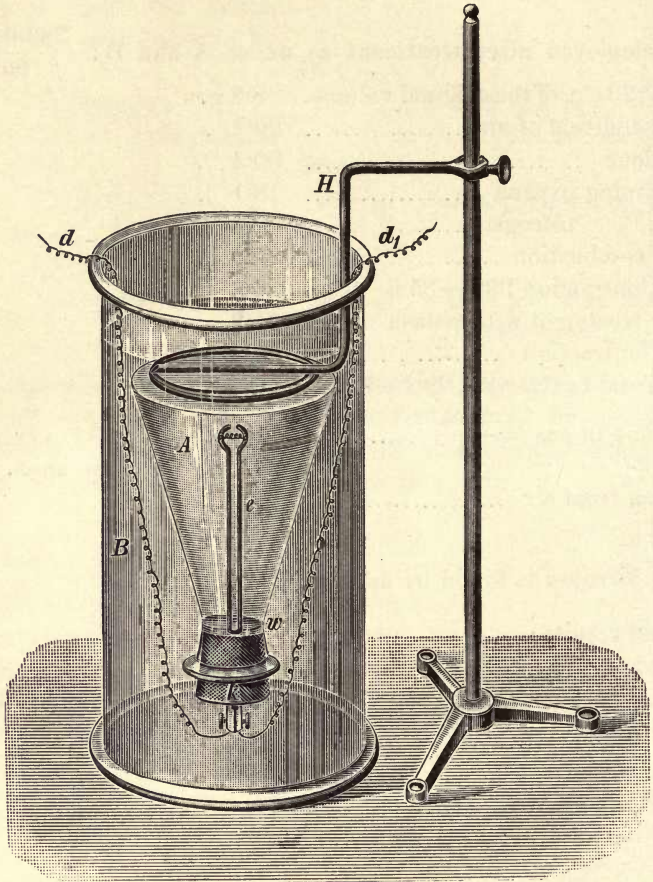
inflammable or explosive, and various apparatus have been con-
structed with that object. This is, however, a mistake. The
mining engineer must try to prevent any accumulation of fire-
damp *before* the percentage of methane has reached the lower limit

of explosiveness. By the examination for methane, both in the branch current and in the principal current of air issuing from the pit, he must carefully establish the average composition of the pit-air, as it changes with the progress of working the coal-seams. In all these cases it is necessary to determine comparatively small quantities of methane, such as could not possibly be read off in a gas-burette with any degree of exactness. The following process leads to the desired end in a simple manner. It consists in burning the methane, consumed in a large volume of pit-air, by means of electrically glowing platinum and afterwards estimating the carbon dioxide by titration. This process has been thoroughly tested in the laboratory of the Freiberg Mining Academy; and it has been established there that a stream of induction-sparks, even of considerable length, cannot replace the electrically glowing platinum.

All the operations of measuring, burning, and titrating are carried on in the conical flask *A*, fig. 77, which is turned upside down, as shown in the figure, during the combustion. On its neck it has a circular mark up to which it is ordinarily closed by a twice-perforated india-rubber cork, with glass-rod stoppers. The contents of the flask up to this mark are ascertained by weighing or measuring and are noted on the glass by etching; it ought to hold about two litres, but in the case of gases containing much methane one litre is sufficient.

When the flask has to serve for a combustion, its stopper is taken out under water and replaced by an india-rubber cork *k*, with electrode *e*. It possesses a second perforation, closed by a short glass rod, for the purpose of introducing by means of a pipette a certain volume of water, say 10 c.c. This water prevents during the combustion the contact of the gas with the india-rubber, which might produce considerable errors; when turning the flask upside down, it forms the protecting layer *w*. Its volume must be known, as well as that of the electrode *e*, and these amounts must be deducted from the contents of flask *A*.

Lest the flask should get hot during the combustion, it is immersed in a beaker filled with water and prevented from rising up by means of the adjustable iron holder *H*, as shown in the figure. If the beaker is replaced by a tin vessel, the holder can be fixed to its side. Wires *d* and d_1, which transmit the electric current, should be at least 1 mm. thick and insulated with gutta-percha.

The electrode e, shown half-size in fig. 78, has been constructed by O. Brunck [*]. It is made of brass and must not be varnished, to avoid any organic substance. Its parallel arms a and a_1 at the top form an open ring b which carries, by means of screws, the platinum spiral c and at the same time protects this against a shock. In their lower part the two arms are insulated by a strong strip of india-rubber, and at the bottom they form together a cylindrical part d which passes gas-tight through the central opening of the cork of flask A, so that the insulating strip of india-rubber does not project above the protecting layer of water w. The insulating strip is continued down to the end, being thinner there; at the bottom the holes e and e_1 are drilled into the two arms; into these holes the current-wires are introduced and held fast by screws f and f_1. Spiral c consists of platinum wire, 0·35 mm. thick; the total length of wire within the screw-clamps is 7 cm. In order to bring this platinum spiral to a bright red heat without any fear of fusing it, a current of 8 or 9 amperes should be applied, $e.\,g.$, by two large Bunsen elements placed in series, or by two storage-cells.

Fig. 78.

Manipulation.—Flask A is filled with distilled water, carried into the coal-pit, and the water run out on the spot where the sample of gas is to be taken. The flask is closed by its twice-perforated cork and taken into the laboratory. If the sample had been taken in another vessel, $e.\,g.$ the zinc vessel described p. 21, the flask A is filled from this in the laboratory, taking care to let the inlet-tube end at the highest point of the flask, previously filled with water and inverted under water, so that the gas comes into the least possible contact with the water.

The flask A, filled with the gas to be examined, is now closed by the other cork, provided with the electrode e, effecting the exchange of corks under water of the temperature of the room. The pro-
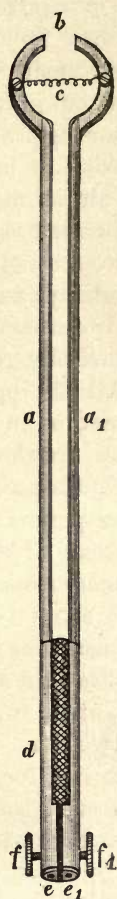
[*] It is sold by Louis Jentzsch, Silbermannstrasse 1, Freiberg in Saxony.

tecting water w is put in, the current-wires d and d_1 are attached, the flask is placed under the water contained in B and fixed by holder H. Now the current is closed and the platinum spiral kept at a bright red heat for half an hour, in order to burn the methane completely by the oxygen always present in excess. Then the current is interrupted, the electrode-cork is replaced by the ordinary cork, and the carbon dioxide titrated as described pp. 49 & 105. As a rule, the baryta-water can be run in from the burette without raising the cork. The volume of gas employed must be reduced to normal conditions.

Application as above described for *pit-air and other non-inflammable mixtures, containing relatively little methane.* Heavy hydrocarbons and carbon monoxide must be absent. Carbon dioxide is rarely absent; it is estimated by titration in another sample of gas by Hesse's method (p. 103), and deducted from the total CO_2 found after combustion.

EXAMPLE.—Pit-air. The reduction apparatus (p. 26) shows 112·8 c.c.

A. *Estimation of carbon dioxide.*

Oxalic acid (gas normal) ...... 1 c.c. $=1$ c.c. CO_2.
Baryta-water titrated .... 1 ,, $=1\cdot03$,, oxalic acid.
$=1\cdot03$,, CO_2.
Contents of absorption-bottle......... 622 ,,
Baryta-water employed .... 10 ,, $=10\cdot3$ c.c. CO_2.
Gas analyzed $622-10$ .... $=612$,,
Corrected $\left(\dfrac{100\times612}{112\cdot8}\right)$ .... 542 ,,
Oxalic acid required for retitrating . 8·5 ,,
Oxalic acid equivalent to 10 c.c.
baryta-water.......................... 10·3 ,,
Difference $10\cdot3-8\cdot5$ .... $=1\cdot8$,, $=0\cdot33$ p.c. CO_2.

B. *Estimation of methane.*

Contents of absorption-bottle... 2000 c.c.
    less protecting water 10
        contents of electrode 6
        baryta-water added
        after combustion ...20
                    —— 36 c.c.

Gas really employed for test ... 1964 c.c.
     Corrected .... 1741 ,,
20 c.c. baryta-water required... 20·6 ,, normal oxalic acid.
Employed for retitrating........ 4·3 ,,   ,,   ,,
     Difference......... 16·3 ,,   ,,   ,,
             = 0·93 p.c. CO_2 p. vol.
Deduct CO_2 found *sub* A... 0·33 p.c.   ,,
Leaving as methane........ 0·60 p.c. CH_4.

d. Drehschmidt's Platinum-Capillary.

The just described method requires an electric current which, if it has to be specially produced, makes the apparatus quite as complicated as that required for the explosion method. This is avoided by the following method.

Already Orsat ('Note sur l'Analyse industrielle des Gaz,' Paris, 1887) noticed that methane, mixed with air or even with pure oxygen, can be burned without loss or danger in a capillary tube made of platinum. This observation was taken up and enlarged by Drehschmidt (Berl. Berichte, 1888, xxi. p. 3242). The possibility of employing pure oxygen, and therefore avoiding the dilution with nitrogen, admits of employing a larger volume of gas. The oxygen need not be absolutely pure, especially from nitrogen; it can be made as usual from potassium chlorate, and after careful washing kept for use in a gas-holder.

Drehschmidt's capillary is a platinum tube, 200 mm. long, 2 mm. thick, 0·7 mm. bore, and at both ends soldered to brass connections. In order to avoid explosions, it is nearly filled up all along by two or three thin platinum wires.

The above length is necessary, because otherwise the ends become too hot. This can be avoided, as shown by the author, by cooling the ends with water, fig. 79.

Fig. 79.

The platinum tube proper, *p*, which must not be made by soldering, but bored or drawn, is 2·5 or 3 mm. wide, 0·7 mm. bore,

and only 100 mm. long, and is filled with several thin platinum wires in such manner that the gas passes through without sensible resistance. To its ends are soldered the copper elbows k and k_1, 5 mm. outside diameter, 1 or 2 mm. bore, equally filled with thin platinum or copper wire. These are surrounded by the copper or brass jackets w and w_1, tubulated at top, 50 mm. long, 25 mm. wide, which receive the cooling water. The whole, in order to be protected against bending &c., rests by means of the washers s and s_1, on a fork movable on a stand, and is heated by a gas-burner with fan-shaped top *.

Fig. 80.
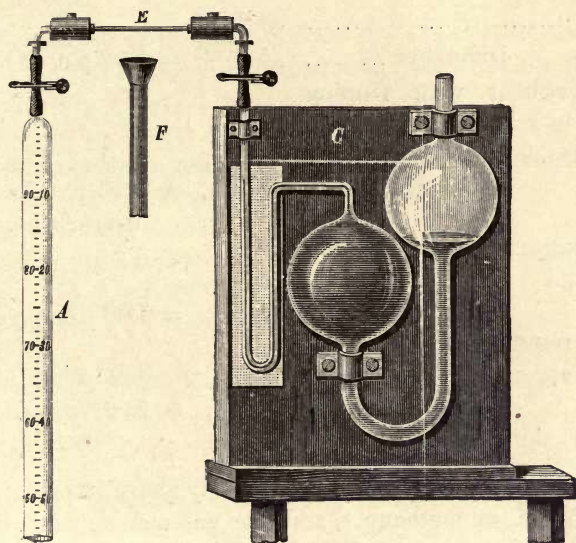
Manipulation.—The gaseous remainder, containing nothing but methane and nitrogen, is transferred into the gas-burette A, fig. 80, a sufficient volume of oxygen is added, the platinum-capillary E interposed between the burette and the gas-pipette C (filled with water), the capillary heated to a bright red heat by means of the gas-burner F; and by opening one pinch-cock entirely, and regulating the other with the right hand, the gas is carried into the pipette and back again in a moderately rapid stream. This operation is

* The capillary and burner are sold by Dr. Robert Muencke, Luisenstrasse 58, Berlin N.W.

repeated once, or at most twice. The capillary is allowed to cool, the contraction is measured, the carbon dioxide removed and the measuring repeated. The methane originally present corresponds to a third of the total contraction observed.

In the case of gases containing very much nitrogen, it is preferable to avoid unnecessary dilution by employing pure oxygen in the previous estimation of hydrogen (by combustion with palladium-asbestos, p. 142) *.

EXAMPLE : *Analysis of producer-gas.*

Gas employed........................ 99·7 c.c.

After treatment with caustic
  potash............................. 93·8 „
           Difference ....   5·9 „ = 5·92 p.c. CO_2.

After treatment with fuming
  sulphuric acid and removal of
  acid vapours by potash .... 93·7 „
           Difference ....   0·1 „ = 0·10 p.c. heavy hydrocarbons.

After treatment with alkaline
  pyrogallol .... 93·7 „
           Difference ....   0·0 „ = 0·00 p.c. oxygen.

After two treatments with ammo-
  niacal cuprous chloride......... 71·5 „
           Difference .... 22·2 „ = 22·27 p.c. CO.
Non-absorbable gaseous remainder 71·5 „

Hydrogen.—Producer-gas contains rarely above 10 p.c. of hydrogen and 5 p.c. of methane †, and the gaseous remainder would therefore require at most $5+10=15$ c.c. oxygen. When em-

---

* It is evident that a Drehschmidt or Winkler platinum-capillary can be attached to the Orsat-Lunge apparatus (fig. 73, p. 147) in place of the palladium-asbestos capillary, *e*, thus enabling that portable apparatus to be used for the estimation of methane. If no regard is taken of the heavy hydrocarbons (which is unnecessary with producer-gas or water-gas), that apparatus is thus capable of performing the entire analysis.— *Translator.*

† Dowson gas and similar " semi-water gas " contains sometimes not much less than 20 p. c. hydrogen, but both this and ordinary producer-gas hardly ever contain 5 p. c. methane.— *Translator.*

ploying the oxygen in the pure state the whole of this remainder can be used for the following operations.

Non-absorbable gas	71·5	c.c.	
After addition of oxygen	94·8	,,	
Oxygen alone	23·3	,,	
After burning with palladium-asbestos...	84·0	,,	
Contraction $94·8 - 84·0$	$= 10·8$	,,	
Hydrogen in the gas $10 \times \frac{2}{3}$	7·2	,,	$= 7·22$ p.c. H.
Oxygen corresponding to this	3·6	,,	
Gaseous remainder	84·0	,,	
Containing oxygen	19·7	,,	

As this oxygen more than suffices for the combustion of the *methane*, the gaseous remainder is at once burned in the platinum capillary, leaving behind .... 78·2 c.c.

Contraction $84·0 - 78·2$	5·8	,,	
After absorption by potash	75·3	,,	
Difference	2·9	,,	
Total contraction $84·0 - 75·3$	8·7	,,	
Corresponding to methane	2·9	,,	$= 2·91$ p.c. CH_4.
,, ,, oxygen	5·8	,,	

Nitrogen.

The non-absorbable gas .... $= 71·5$ c.c.

Contains hydrogen .... 7·2 c.c.

methane .... 2·9

together .... 10·1 ,,

leaving a remainder of .... 61·4 ,, $= 61·58$ p. c. N.

Final result :—

Carbon dioxide	5·92	p. c. by volume.	
Heavy hydrocarbons	0·10	,,	,,
Carbon monoxide	22·27	,,	,,
Hydrogen	7·22	,,	,,
Methane	2·91	,,	,,
Nitrogen	61·58	,,	,,

100·00

2. *Estimation of nitrous oxide by burning with hydrogen.*—If a mixture of nitrous oxide and excess of hydrogen is passed through a (moderately) heated tube, the reaction is: $N_2O + 2H = 2N + H_2O$. This means that 2 vols. $N_2O + 2$ vols. H furnish 2 vols. N (the H_2O being condensed to liquid water), and that the contraction is $= \frac{1}{2}$, or $=$ the volume of the nitrous oxide present. This method might be applied to estimating N_2O in gases containing no other constituents acting upon hydrogen, as oxygen, nitric oxide, &c., and it might be carried out by means of a moderately heated platinum-capillary.

3. *Estimation of nitric oxide by burning with hydrogen.*—This can be carried out (Knorre & Arndt, Berl. Ber. 1899, xxxii. p.2136; 1900, xxxiii. p. 32) as just proposed for N_2O, but the passage of the gas must be slow, to avoid the formation of ammonia. The reaction is: $NO + 2H = N + H_2O$; hence 2 vols. $NO + 2$ vols. H $=$ 1 vol. N ; the contraction is therefore $4 - 1 = 3$, and the volume of nitric oxide is found by multiplying the contraction by $\frac{2}{3}$.

D. *Combustion of Gases by means of hot Copper Oxide.*

This method has been worked out by Fresenius (Zeitschr. f. anal. Chem. 1864, p. 339) at a time when there were no simple gas-analytical methods extant for the estimation of combustible gases. The same principle is even now useful, and indeed indispensable, for the detection of *minimal percentages of combustible gas* ; and it has been employed with full success for many years past by the author, and in other laboratories, for transforming the methane of pit-air into carbon dioxide, to be estimated by titration. It can be applied to indefinitely large quantities of gas, and correspondingly small percentages of combustible gas can be thus estimated. The method will be best understood by the description of the following apparatus, fig. 81, which has been thoroughly tested for the examination of pit-air for methane.

The gas is brought into the laboratory in a zinc 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

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* Hankus (Oesterr. Zsch. f. Berg- und Hüttenwesen, 1897, p. 548) counsels the employment of glass vessels only, because the organic substance attached to the inside of the metal vessels might cause the methane to be transferred into CO_2. This is contrary to the chemical behaviour of methane and to the experience obtained at Freiberg.
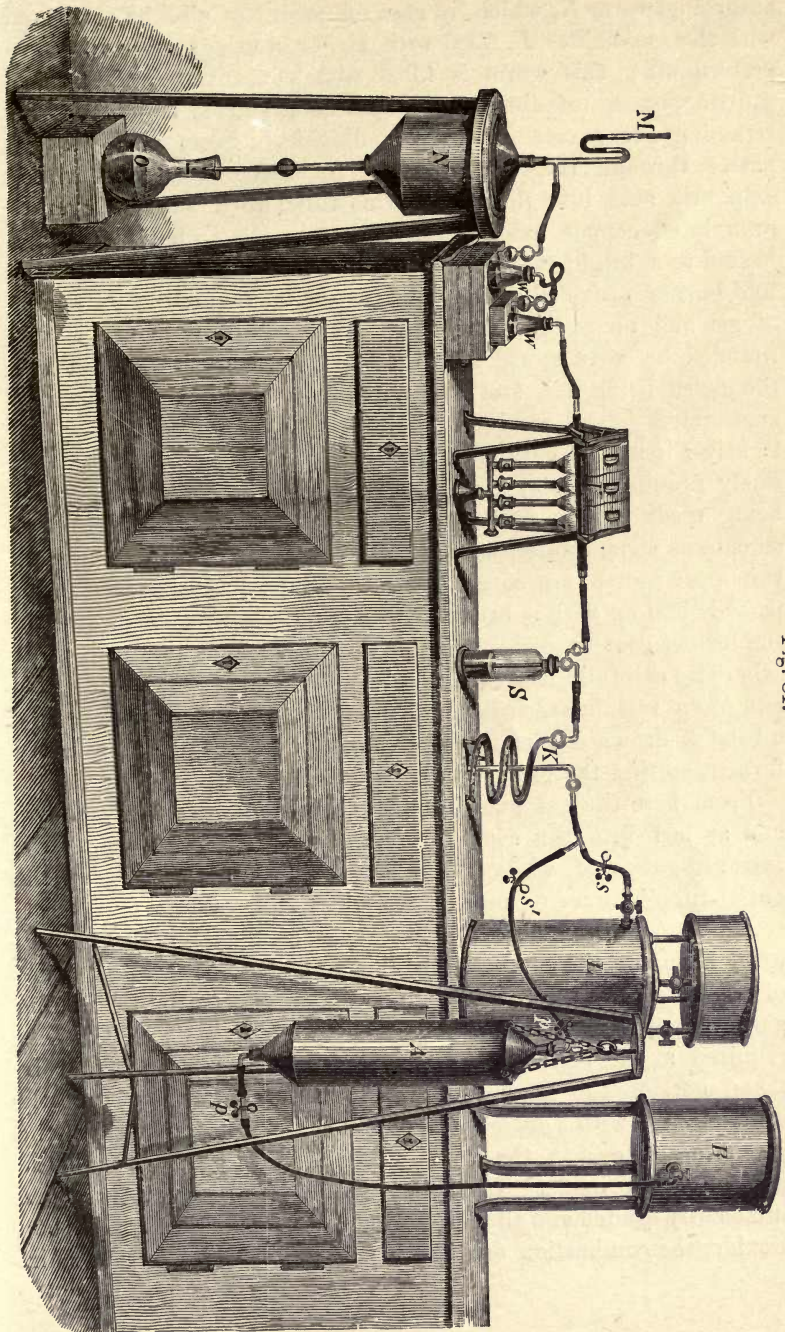
Fig. 81.

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 covered on the outside with a thick paste of finely ground fire-clay mixed with a little pipe-clay (the whole being made into a paste by means of commercial solution of silicate of soda, diluted with four volumes of water), so that only the upper fourth, not covered with wire gauze, remains free. The paste is laid on with a brush in three coats, waiting each time for the former coat to dry. Combustion-tubes thus guarded, when otherwise carefully heated up and cooled down, are very durable and often remain serviceable for months. In lieu of a glass tube a tube of drawn copper might be used, of twice the length of the former, so that the projecting ends remain cool.

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 lighter flask O is placed below the outlet-tube in order to measure the water run out.

Manipulation.— Before making a gas combustion, the copperoxide filling of the combustion-tube must be ignited in a current of air, until clear baryta-water is no longer affected by the issuing gas, even after passing for some time. This air (as well as that required at the end for sweeping out the apparatus) should be taken outside the laboratory, since the laboratory air is mostly contaminated with a little coal-gas which would be detected by the precipitate formed in the baryta-water after passing through the red-hot copper oxide. 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 pinch-cock 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 pinch-cock 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 pinch-cock *p*, and *p'* is connected with the outlet-pipe of the vessel *B*, after having been filled with water. The pinch-cocks *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 pinch-cock *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 phenolphthalein; this quantity is measured off by a burette provided with a float and divided in $\frac{1}{10}$ 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 200 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 litre-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 are now and then 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 pinch-cock 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 sweeping-out. The aspirator-tap is once more opened, and air is drawn through the apparatus, by opening the pinch-cock 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 method, when carefully carried out, yields very accurate results, and admits of estimating the smallest quantities of methane.

Application :—

Estimation of methane in fire-damp and in the up-cast currents of coal-pits and other gaseous mixtures containing very little methane ; estimation of all carbon compounds, combustible to carbon dioxide, as carbon monoxide, hydrocarbons, coal-gas, empyreumatic products, benzene, carbon disulphide, carbon oxysulphide when present in small quantities in the air of dwelling-houses, factories, drying-stoves, heating-apparatus, &c.

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.c.

Found :

$$\frac{100n}{n+m} = \frac{100 \times 11\cdot1}{11\cdot1 + 3422\cdot5} = 0\cdot323 \text{ per cent. methane by volume.}$$

Of course the process as described may be modified in various directions, according to the object aimed at. Thus the gas may be transported in a glass vessel, or brought into the apparatus directly from the place where it is generated. Where carbon disulphide is present it may be removed by interposing between

the copper oxide and the baryta-water a heated layer of lead chromate.   Where there are several compounds present which furnish carbon dioxide on combustion, and the object is to estimate the total contamination caused by them, it is necessary to have an idea of their relative quantities.   If, for instance, the contamination of a room by coal-gas is to be estimated, we must consider that the average composition of coal-gas is as follows, for 100 vols. of gas :—

4	vols.	ethylene gas,	burned to	8	vols. CO_2.
1	,,	benzene vapour	,,	,,	6	,,	,,
8	,,	carbon monoxide,	,,	,,	8	,,	,,
35	,,	methane,	,,	,,	35	,,	,,

48 vols.   burned to 57 vols. CO_2.

Hence 1 c.c. of carbon dioxide found corresponds to 1·75 c.c. coal-gas.

APPENDIX.

1. *International Atomic Weights, as fixed for* 1902 *by the German Chemical Society.*

		O=16 H=1·008	H=1 O=15·88			O=16 H=1·008	H=1 O=15·88
Aluminium	Al	27·1	26·9	Neodymium	Nd	143·6	142·5
Antimony	Sb	120	119·1	Neon	Ne	20	19·9
Argon	A	39·9	39·6	Nickel	Ni	58·7	58·3
Arsenic	As	75·0	74·4	Niobium	Nb	94	93·3
Barium	Ba	137·4	136·4	Nitrogen	N	14·04	13·93
Beryllium	Be	9·1	9·03	Osmium	Os	191	189·6
Bismuth	Bi	208·5	206·9	Oxygen	O	16	15·88
Boron	B	11	10·9	Palladium	Pd	106	105·2
Bromine	Br	79·96	79·36	Phosphorus	P	31·0	30·77
Cadmium	Cd	112·4	111·6	Platinum	Pt	194·8	193·3
Cæsium	Cs	133	132	Potassium	K	39·15	38·86
Calcium	Ca	40·1	39·8	Praseodymium	Pr	140·5	139·4
Carbon	C	12·00	11·91	Rhodium	Rh	103·0	102·2
Cerium	Ce	140	139·	Rubidium	Rb	85·4	84·76
Chlorine	Cl	35·45	35·18	Ruthenium	Ru	101·7	100·9
Chromium	Cr	52·1	51·7	Samarium	Sa	150	148·9
Cobalt	Co	59·0	58·56	Scandium	Sc	44·1	43·8
Copper	Cu	63·6	63·1	Selenium	Se	79·1	78·5
Erbium	Er	166	164·8	Silicon	Si	28·4	28·2
Fluorine	F	19	18·9	Silver	Ag	107·93	107·12
Gadolinium	Gd	156	155	Sodium	Na	23·05	22·88
Gallium	Ga	70	69·5	Strontium	Sr	87·6	86·94
Germanium	Ge	72	71·5	Sulphur	S	32·06	31·83
Gold	Au	197·2	195·7	Tantalium	Ta	183	181·6
Helium	He	4	4	Tellurium	Te	127·6	126·6
Hydrogen	H	1·008	1	Thallium	Tl	204·1	202·6
Indium	In	114	113·1	Therium	Th	232·5	230·8
Iodine	I	126·85	125·90	Thulium	Tu	171	170
Iridium	Ir	193·0	191·5	Tin	Sn	118·5	117·6
Iron	Fe	55·9	55·5	Titanium	Ti	48·1	47·7
Krypton	Kr	81·8	81·2	Uranium	U	239·5	237·7
Lanthanium	La	138	137	Vanadium	Va	51·2	50·8
Lead	Pb	206·9	205·35	Wolframium	W	184	182·6
Lithium	Li	7·03	6·98	Xenon	X	128	127
Magnesium	Mg	24·36	24·18	Ytterbium	Yb	173	172
Manganese	Mn	55·0	54·6	Yttrium	Y	89	88·3
Mercury	Hg	200·3	198·8	Zinc	Zn	65·4	64·9
Molybdenum	Mo	96·0	95·3	Zirconium	Zr	90·7	90·0

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

Name of the gas.	Molecular formula.	1 litre of the gas in the normal state weighs.
		grams
Acetylene	C_2H_2	1·16148
Air (atmospheric)	......	1·29315
Ammonia	H_3N	0·76163
Antimoniuretted hydrogen	H_3Sb	5·6040
Arseniuretted hydrogen	H_3As	3·48801
Benzene	C_6H_6	3·48563
Bromine	Br_2	7·14259
Butane	C_4H_{10}	2·59161
Butylene	C_4H_8	2·50355
Carbon monoxide	CO	1·25058
Carbon dioxide	CO_2	1·96519
Carbon disulphide	CS_2	3·40098
Carbon oxychloride	$COCl_2$	4·41799
Carbon oxysulphide	COS	2·68250
Chlorine	Cl_2	3·16742
Cyanogen	$(CN)_2$	2·32653
Ethane	C_2H_6	1·34058
Ethylene	C_2H_4	1·25103
Fluorine	F_2	1·70684
Hydrogen	H_2	0·08955
Hydrogen bromide	HB	3·61607
Hydrogen chloride	HCl	1·62848
Hydrogen cyanide	HCN	1·2091
Hydrogen fluoride	HF	0·89820
Hydrogen iodide	HI	5·71067
Hydrogen sulphide	H_2S	1·52147
Methane	CH_4	0·71506
Nitrogen	N_2	1·25461
Nitrogen protoxide	N_2O	1·96923
Nitric oxide	NO	1·34192
Nitrogen trioxide (hypothetical)	N_2O_3	3·38051
Nitric peroxide *	NO_2	2·05054
Nitrosyl chloride	$NOCl$	2·92563
Oxygen	O_2	1·42923
Phosphoretted hydrogen	H_3P	1·52058
Propane	C_3H_8	1·96727
Propylene	C_3H_6	1·87654
Silicon tetrafluoride	SiF_4	4·68083
Sulphur dioxide	SO_2	2·86115
Water	H_2O	0·80458

* 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 base of the formula NO_2.

3. *Solubility of Gases in Water.*

1 vol. water of 20° C. absorbs the following volumes of gases, reduced to 0° C. and 760 mm. barometric pressure :—

Air, atmospheric	0·01869
Ammonia	654·0
Carbon monoxide	0·02319
Carbon dioxide	0·90140
Chlorine	2·15650
Ethane........................... ..	0·04724
Ethylene	0·14880
Hydrogen	0·01819
Hydrogen chloride	445·0
Hydrogen sulphide..............	2·90530
Methane	0·03308
Nitrogen	0·01542
Nitrogen protoxide...............	0·06700
Nitrogen oxide	0·04706
Oxygen	0·03103
Propylene	0·22050
Sulphur dioxide	39·374

4. Changes of Volume when Gases are burnt in Oxygen.

Name of gas.	Molecular formula.	Combustion requires		Combustion yields		Volume of gas			Contraction			
		combustible gas.	oxygen.	aqueous vapour (condensed).	carbon dioxide.	before combustion.	after combustion.	after combustion and absorption of carbon dioxide.	after combustion.	ratio of combustible gas to contraction.	after combustion and absorption of CO_2.	ratio of combustible gas to contraction.
		vols.	vols.	vols.	vols.	vols.	vols.	vols.	vols.		vols.	
Acetylene	C_2H_2	2	5	2	4	7	4	0	3	$\frac{2}{3}$	7	$\frac{2}{7}$
Benzene	C_6H_6	2	15	6	12	17	12	0	5	$\frac{2}{5}$	17	$\frac{2}{17}$
Butane	C_4H_{10}	2	13	10	8	15	8	0	7	$\frac{2}{7}$	15	$\frac{2}{15}$
Butylene	C_4H_8	2	12	8	8	14	8	0	6	$\frac{1}{3}$	14	$\frac{1}{7}$
Carbon monoxide	CO	2	1	...	2	3	2	0	1	2	3	$\frac{2}{3}$
Ethane	C_2H_6	2	7	6	4	9	4	0	5	$\frac{2}{5}$	9	$\frac{2}{9}$
Ethylene	C_2H_4	2	6	4	4	8	4	0	4	$\frac{1}{2}$	8	$\frac{1}{4}$
Hydrogen	H_2	2	1	2	...	3	0	...	3	$\frac{2}{3}$	...	...
Methane	CH_4	2	4	4	2	6	2	0	4	$\frac{1}{2}$	6	$\frac{1}{3}$
Propane	C_3H_8	2	10	8	6	12	6	0	6	$\frac{1}{3}$	12	$\frac{1}{6}$
Propylene	C_3H_6	2	9	6	6	11	6	0	5	$\frac{2}{9}$	11	$\frac{2}{11}$

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

for 1 kilogram of substance, expressed in calories, one of which
= the heating of 1 kilogram 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.
Calcium, CaO	CaO	3,284·0	Favre and Silbermann.
Carbon: wood-charcoal	CO	2,473·0	„ „
„ „	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)	11,967·1	„
„	$2CO_2+2H_2O$ (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	„

Table (*continued*).

1 kilog. substance.	Burning to	Gives off calories.	Observer.
Nitrogen monoxide, N_2O	NO	$-\ 564\cdot3$	Thomsen.
Nitric oxide, NO	NO_2	$652\cdot3$	,,
Phosphorus	P_2O_5	$5,964\cdot5$	,,
Potassium	K_2O	$1,745\cdot0$	Woods.
Propane	$3CO_2+4H_2O$ (liquid)	$12,125\cdot0$	Thomsen.
,,	$3CO_2+4H_2O$ (steam)	$11,136\cdot3$	,,
Propylene, C_3H_6	$3CO_2+3H_2O$ (liquid)	$11,790\cdot4$	,,
,,	$3CO_2+3H_2O$ (steam)	$11,019\cdot0$	,,
Silicon	SiO_2	$7,830\cdot0$	,,
Silver	Ag_2O	$27\cdot3$	,,
Sodium	Na_2O	$3,293\cdot0$	Woods.
Sulphur, rhombic	SO_2	$2,221\cdot3$	Thomsen.
,, monoclinic	....	$2,241\cdot4$	,,
Sulphuretted hydrogen	SO_2+H_2O (liquid)	$2,741\cdot0$	Favre and Silbermann.
,, ,,	SO_2+H_2O (steam)	$2,457\cdot0$	,, ,,
Tin	SnO	$573\cdot6$	Andrews.
,,	SnO_2	$1,147\cdot0$	,,
Zinc	ZnO	$1,314\cdot3$	Thomsen.

6. *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	grams 2·1807 Sulphuric acid	SO_4H_2
,,	,,	2·5075 Potassium hydroxide	KOH
Carbon monoxide	CO	5·6296 Oxalic acid, crystallized	$C_2H_2O_4$, $2H_2O$
,, ,,	,,	14·0943 Barium hydroxide, cryst.	$Ba(OH)_2$, $8H_2O$
Carbon dioxide	CO_2	5·6296 Oxalic acid, crystallized	$C_2H_2O_4$, $2H_2O$
,, ,,	,,	14·0943 Barium hydroxide, cryst.	$Ba(OH)_2$, $8H_2O$
Chlorine	Cl	4·4216 Arsenious acid, dissolved in sodium bicarbonate	As_2O_3
,,	,,	11·3353 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.	
		grams	
Hydrogen chloride...	HCl	4·8215 Silver, dissolved in nitric acid	Ag
,, ,, ...	,,	3·4028 Ammonium sulphocya-nide	CNS, NH₄
,, ,, ...	,,	2·5075 Potassium hydroxide...	KOH
Methane	CH₄	5·6296 Oxalic acid, crystalized	C₂H₂O₄, 2H₂O
,, ...	,,	14·0943 Barium hydroxide cryst.	Ba(OH)₂, 8H₂O
Nitrogen trioxide ...	N₂O₃	5·6230 Potassium permanga-nate	KMnO₄
Nitrogen oxide	NO	4·2406 ,, ,,	,,
Sulphur dioxide ...	SO₂	11·3353 Iodine in Potassium iodide	I
		5·0166 Potassium hydroxide...	KOH

7. *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 :—

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* For permanent laboratory use G. Lunge has published tables, to be hung on the wall, for reducing gas-volumes to normal conditions and for gas-volumetric analysis (Brunswick, 1897).

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

$$\overline{\qquad\qquad\qquad}$$

$$0 \cdot 89703848$$

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	

TECHNICAL GAS-ANALYSIS.

Table (*continued*).

Temperature 0° 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 0° 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 0° 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 0° 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_0	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.