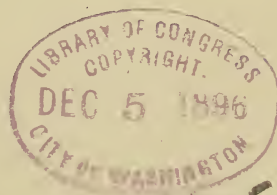# GAS AND FUEL ANALYSIS
FOR ENGINEERS.

A COMPEND FOR THOSE INTERESTED IN THE ECONOMICAL APPLICATION OF FUEL.

PREPARED ESPECIALLY FOR THE USE OF STUDENTS
at the
MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

BY

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PREFACE.

THIS little book is an attempt to present in a concise yet clear form the methods of gas and fuel analysis involved in testing the efficiency of a boiler plant. Its substance was given originally, in the form of lectures and heliotyped notes, to the students in the courses of Chemical, Mechanical, and Electrical Engineering, but in response to requests it has been deemed expedient to give it a wider circulation.

At the time of its conception, nothing of the kind was known to exist in the English language; in German we now have the excellent little book of Dr. Ferdinand Fischer, "Taschenbuch für Feuerungs-Techniker."

The present book is the result of six years' experience in the instruction of classes of about one hundred students. It is in no sense a copy of any other work, nor is it a mere compilation. The author has in every case endeavored to give credit where anything has been taken from outside sources; it is, how-

ever, difficult to credit single ideas, and if he has been remiss in this respect it has been unintentional.

The study of flue-gas analysis enables the engineer to investigate the various sources of loss; and if this compend stimulates and renders easy such investigation, the writer's purpose will have been accomplished. The necessary apparatus can be obtained from the leading dealers in New York City.

The author wishes to acknowledge his indebtedness to our former Professor of Analytical Chemistry, Dr. Thomas M. Drown, and to Mrs. Ellen H. Richards, by whose efforts the department of Gas Analysis was established.

He will also be grateful for any suggestions or corrections from the profession.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
    BOSTON, November, 1896.

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GAS AND FUEL ANALYSIS.

CHAPTER I.

INTRODUCTION AND METHODS OF SAMPLING.

UNTIL within recent years, the mechanical engineer in testing a boiler plant has been compelled to content himself with the bare statement of its efficiency, little or no idea being obtained as to the apportionment of the losses. Knowing the composition and temperature of the chimney-gases and the analysis of the coal and ash, the loss due to the formation of carbonic oxide, to the imperfect combustion of the coal, to the high temperature of the escaping gases, can each be determined and thus a basis for their reduction to a minimum established.

By the simple analysis of the chimney-gases and determination of their temperature, a very good idea of the efficiency of the plant can be obtained previous to making the engineering test. For example, in a test which the author made in connection with his students, the efficiency was increased from 58 to 70 per cent, upon the results of the gas analysis alone.

To this end a representative sample must be collected according to the method about to be described.

<center>SAMPLING.</center>

Before proceeding to take a sample of the gas, the plant—for example, a boiler setting—from which the gas is to be taken should be thoroughly inspected, and all apertures by which the air can enter, carefully stopped up. A suitable tube is then inserted air-tight in the gas-duct, connected with the sampling or gas apparatus, and suction applied, thus drawing the gas out. Cork, putty, plaster of Paris, wet cotton-waste, or asbestos may be used to render the joint gas-tight. The place of insertion should be chosen where the gas will be most completely mixed and least contaminated with air. The oil-bath containing the thermometer is similarly inserted near the gas-tube, and the temperature read from time to time.

1. Tubes.—The tubes usually employed are Bohemian-glass combustion tubing or water-cooled metal tubes; those of porcelain or platinum are also sometimes used. Glass and porcelain tubes when subjected to high temperatures must be previously warmed or gradually inserted: the former may be used up to temperatures of 600° C. (1200° F.). Uncooled metal tubes, other than those of platinum, should under no circumstances be used.*

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* Fischer, "Technologie der Brennstoffe," 1880, p. 221, states that the composition of a gaseous mixture was changed from 1.5 to 26.0 per cent carbon dioxide, by the passage through an iron tube heated to a dull red heat, the carbonic oxide originally present reducing the iron oxide with the formation of carbon dioxide.

The metal tube with the water cooling is made as shown in Fig. 1, *c* being a piece of brass pipe 3 feet long, $1\frac{1}{4}$ inches outside diameter, *b* the same length, $\frac{7}{8}$ inch in diameter, and *a* $\frac{1}{4}$ inch in diameter. The water enters at *d* and leaves at *e*. The walls of
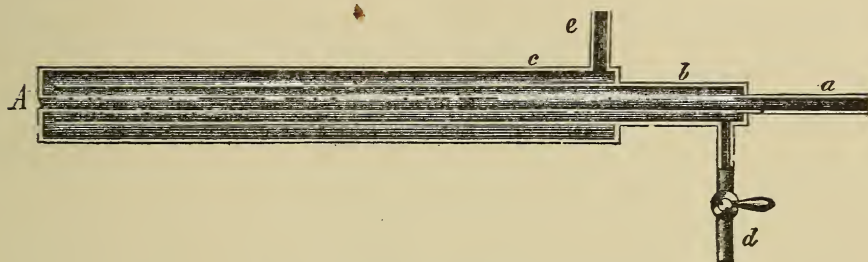
FIG. 1.—GAS-SAMPLING TUBE.

the tubes are $\frac{1}{16}$ inch thick. The joint at *A* should be brazed; the others may be soldered.

Platinum tubes from their high cost and small bore are seldom used; they are attacked by carbon, cyanogen, arsenic, and metallic vapors.

2. **Apparatus for the Collection of Samples.—** A convenient sampling apparatus is shown in Fig. 2. It may be made from a liter separatory funnel—instead of the bulb there shown—fitted with a rubber stopper carrying a tube passing to the bottom and a T tube; both of these, except where sulphur-containing gases are present, can advantageously be made of $\frac{3}{16}$-inch lead pipe. The stopper should not be fastened down with wire between the tubes after the manner of wiring effervescent drinks, as this draws the rubber away from the tubes and occasions a leak. The fastening shown consists of a brass plate fitting upon the top of the stopper, provided with screws and nuts which pass through a wire around

the neck of the separatory. A chain fastened to the
plate serves as a convenient method of handling it.

In using the apparatus, the bulb is filled with water
by connecting the stem with the water-supply and
opening one of the pinchcocks upon the T tube; the
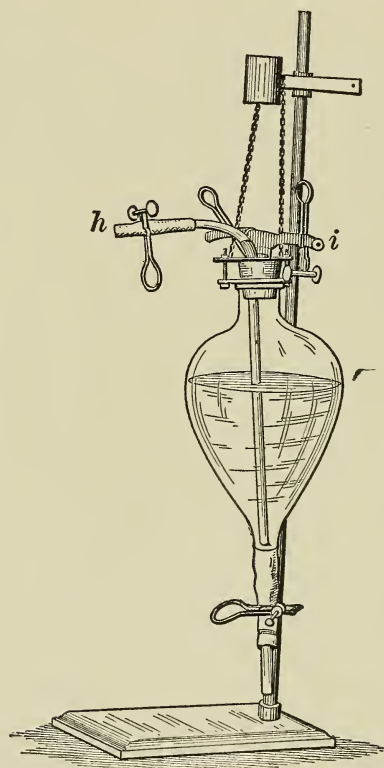
FIG. 2.—SAMPLING APPARATUS.

water thus entering from the bottom forces the air
out before it.   One branch of the T is connected with
the sampling-tube and the other with the suction-
pump, the stopcocks being open, and a current of gas
drawn down into the pump; upon opening the cock
upon the stem, the water runs out, drawing a small
portion of the gas-current passing through the T after
it into the bulb.   It is then taken to a convenient

place for analysis, the tube *h* connected with a head of water, a branch of the T *i*, with the gas apparatus, and a sample of gas forced over into the letter for analysis.
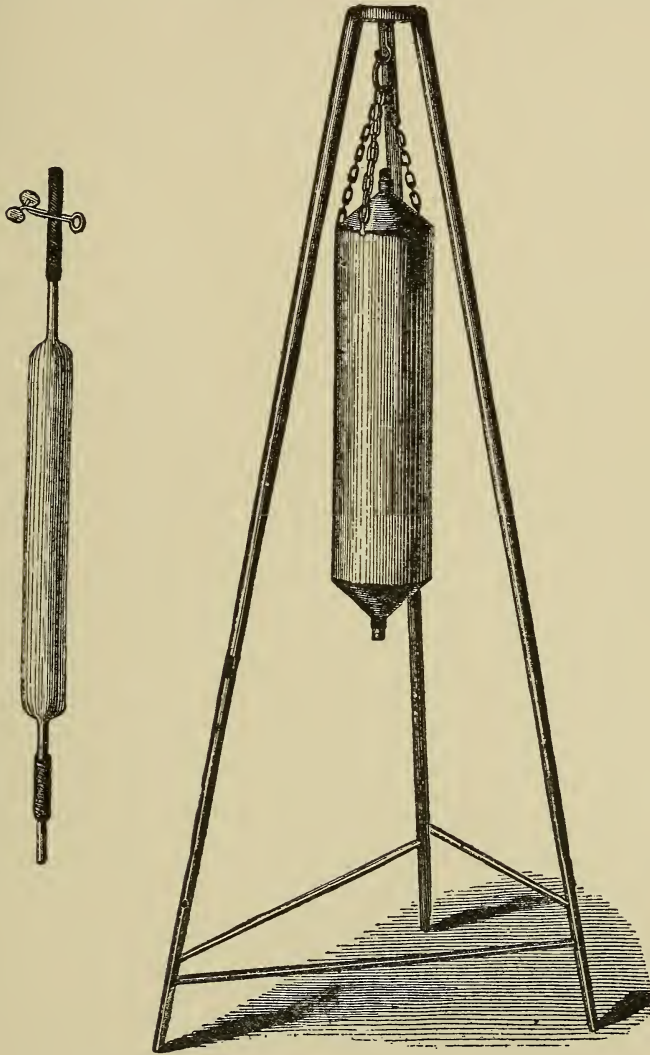
FIG. 4.—GAS-TUBE. FIG. 3.—SAMPLING APPARATUS FOR MINE-GASES.

Enough water should be left in the bulb to seal the stopcock on the bottom and prevent leakage. This apparatus is better adapted for the needs of the class-

room than for actual practice, as it enables the same sample to be given to eight or ten students. As has been shown by several years' experience, the water exercises no appreciable solvent action upon the gaseous mixture in the time—about half an hour— necessary to collect and distribute the samples. It is often necessary to attach about a yard of $\frac{1}{4}$-inch rubber tubing to the stem of the bulb to prevent air being sucked up through it when taking a sample.

In the actual boiler-test it is preferable to insert a T instead of this apparatus in the gas-stream, connect the gas apparatus to the free branch of this T, and draw the sample. In making connections with gas apparatus the air in the rubber connectors should be displaced with water by means of a medicine-dropper.

In the Saxon coal-mines, zinc cans of ten liters capacity, of the form shown in Fig. 3, are used by Winkler for sampling the mine-gases; they are carried down filled with water and this allowed to run out, and the gas thus obtained brought into the laboratory and analyzed. Small samples of gas may very well be taken in tubes of 100 cc. capacity like Fig. 4, the ends of which are closed with rubber connectors and glass plugs. Rubber bags are not to be recommended for the collection and storage of gas for analysis, as they permit of the diffusion of gases, notably hydrogen.

3. **Apparatus for Producing Suction.**—I. WATER-PUMPS—(*a*) Jet-pumps, depending for their action upon a considerable head of water, and (*b*) those depending rather upon a sufficient fall of water.

(*a*) *Jet-pumps.*—The Richards' jet pump [*] is shown in section in Fig. 5 and much resembles a boiler injector; it consists of a water-jet *w*, a constriction or waist *a*, a waste-tube *o*, and a tube for the inspiration of air. The jet of water forms successive pistons across *a*, drawing the air in with it and is broken up into foam by the zigzag tube *o*.

This pump is known in Germany as Muencke's, and in England as Wing's; Chapman's pump is also a modified form.

It may be easily constructed in glass, the jets passing through rubber stoppers which are wired down, thus admitting of adjustment to the conditions under which it has to work.

(*b*) *Fall-pumps.*—Bunsen's pump, Fig. 6, consists of a wide glass tube *A*, drawn out at the bottom for connection with a ¼-inch lead pipe *b*, and at the top for connection with *c*, the tube through which the air is drawn; this tube is usually fused in, although it may be connected with rubber; *a* is a rubber tube provided with screw cocks connected with the water-supply; *d* is connected with a mercury column, and the vessel *B* serves for the retention of any water which might be drawn back into the apparatus evacuated.

The tube *b* for the best results should be 32 feet in length, equal to the height of a column of water supported by the atmosphere, although for the ordinary purposes of gas-sampling it may be shorter.

When water is admitted through *a* it fills *b*, acting

* Richards, Am. Jour. of Science (3), **8**, 412; Trans. Am. Inst. Min. Engrs., **6**, 492.

as a continually falling piston drawing the current of
air through *e* and its connections.   These various
forms of water-pumps should give a vacuum repre-
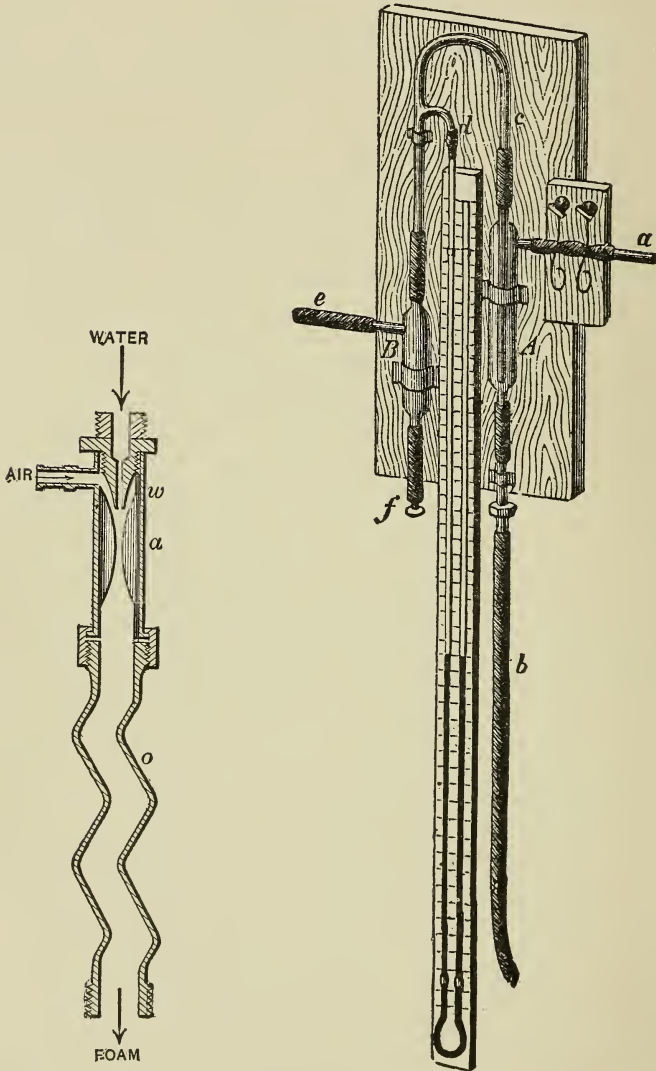
FIG. 5.—RICHARDS' JET-PUMP.   FIG. 6.—BUNSEN'S PUMP.

sented by the height of the barometer less the tension
of aqueous vapor at the temperature at which they
are used, or about 29 inches of mercury.

II. Steam-pumps.—Kochinke describes the appa-
ratus in use in the Muldner Hütten in Freiberg,
shown at one-fifth size in Fig. 7. It consists of a
glass tube drawn down to an opening 6 mm. in diam-
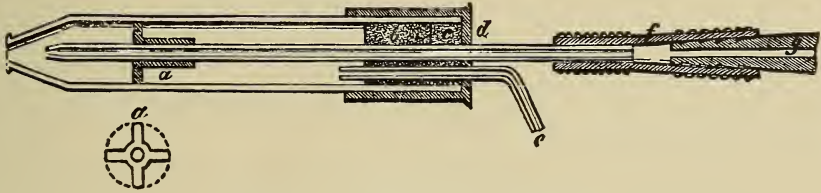
FIG. 7.—STEAM AIR-PUMP.

eter; concentric with this, and held in place by the
washer *a*, is the steam-jet 2 mm. in diameter, passing
through the cork *b*, the cement *c*, and covering *d*. It
is connected with the steam-pipe at *g* by webbed
rubber tubing *f*; the air enters at *e*. This is said to
give very good results and be economical in use of
steam.

In case neither water nor steam be available,
recourse must be had to the ordinary rubber syringe-
bulbs, provided with suitable valves, obtainable at any
rubber store, or to a bottle aspirator. This consists of
two one-gallon bottles, provided with doubly perfor-
ated rubber stoppers, carrying tubes of glass or lead
bent at right angles. In each bottle one of these tubes
passes nearly to the bottom, and these are connected
together by a piece of rubber tubing a yard long,
carrying a screw pinchcock. The other tube in each
case stops immediately under the stopper. Upon
filling one of the bottles with water, inserting the
stopper and blowing strongly through the short tube,
water will fill the long tubes thus forming a siphon,

and upon lowering the empty bottle, a current of air
will be sucked in through the short tube originally
blown into; this may be regulated by the screw
pinchcock.

CHAPTER II.

APPARATUS FOR THE ANALYSIS OF CHIMNEY-GASES.

In the writer's opinion the apparatus which is best adapted for this purpose is that of Orsat; it is readily portable, not liable to be broken, easy to manipulate, sufficiently accurate, and—in the modification about to be described—always ready for use, there being no stopcocks to stick fast.

As the Bunte and Elliott apparatus are also used for this purpose, they too will be described.

Fischer's apparatus, using mercury, is rather too difficult for the average engineer; Hempel's apparatus for the analysis of illuminating-gas might also be used; it is, however, not customary.

ORSAT APPARATUS.

Description.—The apparatus Fig. 8, is enclosed in a case to permit of transportation from place to place; furthermore, the measuring-tube is jacketed with water to prevent changes of temperature affecting the gas-volume. The apparatus consists essentially of the levelling-bottle A, the burette B, the pipettes P', P'', P''', and the connecting tube T.

Manipulation.— The reagents in the pipettes should be adjusted in the capillary tubes to a point on the stem about midway between the top of the pipette and the rubber connector. This is effected by opening wide the pinchcock upon the connector, the
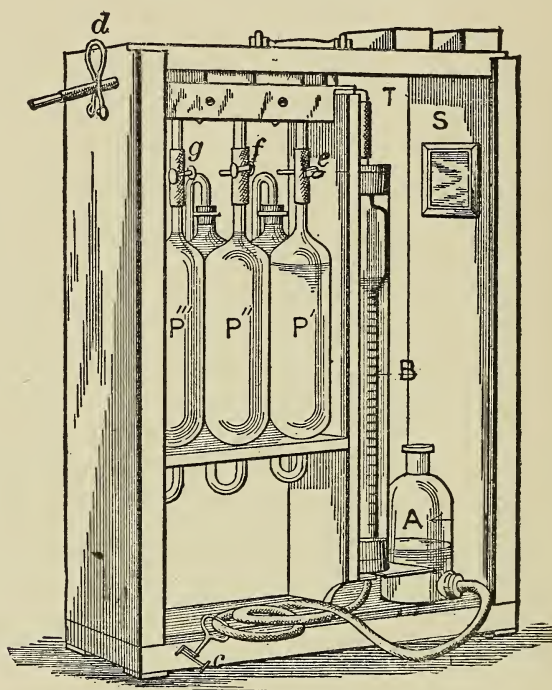
FIG. 8.—ORSAT'S GAS APPARATUS.

bottle being on the table, and very gradually lowering the bottle until the reagent is brought to the point above indicated. Six inches of the tubing used correspond to but 0.1 cc., so that an error of half an inch in adjustment of the reagent is without influence upon the accuracy of the result. The reagents having been thus adjusted, the burette and connecting tube are completely filled with water by opening *d* and raising the levelling-bottle. The apparatus is now

ready to receive a sample of gas (or air for prac-
tice). In case a flue-gas is to be analyzed d is con-
nected with i, Fig. 2, A lowered and about 102 cc.
of the gas forced over by opening h; or d may
be connected with a T joint in the gas-stream; the
burette after filling is allowed to drain one minute by
the sand-glass, c snapped upon its rubber tube, and
the bottle A raised to the top of the apparatus. By
gradually opening c the water is allowed to run into
the burette until the lower meniscus stands upon the
100 or 0 mark (according to the graduation of the
apparatus). The gas taken is thus compressed into
the space occupied by 100 cc., and by opening d the
excess escapes. Open c and *bring the level of the
water in the bottle to the same level as the water in the
burette* and take the reading, which should be 100 cc.
Special attention is called to this method of reading:
if the bottle be raised, the gas is compressed; if
lowered, it is expanded.

Determination of Carbon Dioxide.—The gas to be
analyzed in invariably passed first into pipette P', con-
taining potassium hydrate for the absorption of carbon
dioxide, by opening e and raising A. The gas dis-
places the reagent in the front part of the pipette,
laying bare the tubes contained in it, which being
covered with the reagent present a large absorptive
surface to the gas; the reagent moves into the rear
arm of the pipette, displacing the air over it into the
flexible rubber bag which prevents its diffusion into
the air. The gas is forced in and out of the pipette
by raising and lowering A, the reagent finally brought
approximately to its initial point on the stem of the

pipette, the burette allowed to drain one minute, and the reading taken. The difference between this and the initial reading represents the cubic centimeters of carbon dioxide present in the gas. To be certain that all the carbon dioxide is removed, the gas should be passed a second time into P' and the reading taken as before; these readings should agree within 0.1 per cent.

Determination of Oxygen.—The residue from the absorption of carbon dioxide is passed into the second pipette, P'', containing an alkaline solution of potassium pyrogallate, until no further absorption will take place. The difference between the reading obtained and that after the absorption of carbon dioxide, represents the number of cubic centimeters of oxygen present.

Determination of Carbonic Oxide.—The residue from the absorption of oxygen is passed into the third pipette, P''', containing cuprous chloride, until no further absorption takes place; that is, in this case until readings agreeing exactly (not merely to 0.1) are obtained. The difference between the reading thus obtained and that after the absorption of oxygen, represents the number of cubic centimeters of carbonic oxide present.

Determination of Hydrocarbons. — The residue left after all absorptions have been made may consist, in addition to nitrogen, the principal constituent, of hydrocarbons and hydrogen. Their determination is difficult for the inexperienced, and, if desired, a sample of the flue-gas should be taken, leaving as little water

in the apparatus as possible, and sent to a competent chemist for analysis.

Accuracy.—The apparatus gives results accurate to 0.2 of one per cent.

Time Required.—About twenty minutes are required for an analysis; two may be made in twenty five minutes, using two apparatus.

Notes.—The method of adjusting the reagents is the only one which has been found satisfactory: if the bottle be placed at a lower level and an attempt made to shut the pinchcock c upon the connector at the proper time, it will almost invariably result in failure.

The process of obtaining 100 cc. of gas is exactly analagous to filling a measure heaping full of grain and striking off the excess with a straight-edge; it saves arithmetical work, as cubic centimeters read off represent percent directly.

It often happens when e is opened, c being closed, that the reagent in P' drops, due not to a leak as is usually supposed, but to the weight of the column of the reagent expanding the gas.

The object of the rubber bags is to prevent the access of air to the reagents, those in P'' and P''' absorbing oxygen with great avidity, and hence if freely exposed to the air would soon become useless.

Carbon dioxide is always the first gas to be removed from a gaseous mixture. In the case of air the percentage present is so small, 0.08 to 0.1, as scarcely to be seen with this apparatus. It is important to use the reagents in the order given; if by mistake the gas be passed into the second pipette, it will absorb not only oxygen, for which it is intended, but also carbon

dioxide; similarly if the gas be passed into the third pipette, it will absorb not only carbonic oxide, but also oxygen as well.

The use of pinchcocks and rubber tubes, original with the author, although recommended by Naef,* is considered by Fischer,† to be inaccurate. The experience of the author, however, does not support this assertion, as they have been found to be fully as accurate as glass stopcocks, and very much less troublesome and expensive.

In case any potassium hydrate or pyrogallate be sucked over into the tube T or water in A, the analysis is not spoiled, but may be proceeded with by connecting on water at d, opening this cock, and allowing the water to wash the tubes out thoroughly. The addition of a little hydrochloric acid to the water in the bottle A will neutralize the hydrate or pyrogallate, and the washing may be postponed until convenient.

After each analysis the number of cubic centimeters of oxygen and carbonic oxide should be set down upon the ground-glass slip provided for the purpose. By adding these numbers and subtracting their sum from the absorption capacity (see Reagents) of each reagent, the condition of the apparatus is known at any time, and the reagent can be renewed in season to prevent incorrect analyses.

BUNTE APPARATUS.

Description.—The apparatus Fig. 9 consists of a burette—bulbed to avoid extreme length—provided

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* Wagner's Jahresb. 1885, p. 423.
† Technologie d. Brennstoffe, foot note p. 295,

at the top with a funnel F and three-way cock j, and a cock l at the bottom. These stopcocks are best of the Greiner and Friedrichs obliquely bored form. The burette is supported upon a retort-stand with a spring clamp.

A "suction-bottle" S, an 8-oz. wide-mouthed bottle, fitted similarly to a wash-bottle, except that the delivery-tube is straight and is fitted with a four-inch piece of $\frac{1}{4}$-inch black rubber tubing, serves to withdraw the re-agents and water when necessary. A reservoir to contain water at the temperature of the room, fitted with a long rubber tube, should be provided for washing out the reagents and filling the burette.

Manipulation. — Before using the apparatus, the keys of the stopcocks should be taken out, wiped dry, together with their seats, and sparingly smeared with vaseline or a mixture of vaseline and tallow and replaced. The completeness of the lubrication can be judged by the transparency of the joint, a thoroughly lubricated joint showing no ground glass. The burette is filled with water by attaching the rubber tube to the tip at l and opening the stopcocks at the top and bottom; j is connected with the source whence the gas is to be taken, turned to communicate with the burette and opened, about 102 cc. of gas allowed to run in, and j and l closed.
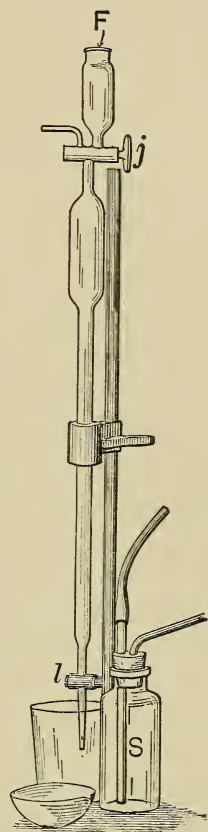
FIG. 9.—BUNTE'S GAS APPARATUS.

The cup F is filled with water to the 25-cc. mark, j turned to establish communication between it and the burette, the burette allowed to drain one minute by the sand-glass, and the reading taken, the cup being refilled to the mark if necessary. The readings are thus taken under the same pressure each time, i.e., this column of water plus the height of the barometer; and as the latter is practically constant during the analysis, no correction need be applied, it being within the limits of error.

Determination of Carbon Dioxide.—The '' suction-bottle '' is connected with the tip of the burette, l opened, and the water carefully sucked out nearly to l. The bottle is now disconnected, the burette dismounted from its clamp, using the cup as a handle, and the 25 cc. of water turned out. The tip is immersed under potassium hydrate contained in the No. 3 porcelain dish, and the cock l opened, then closed, and the tip wiped clean with a piece of cloth. The burette is now shaken, holding it by the tip and the cup, the thumbs resting upon j and l; more reagent is introduced, the absorption of the gas causing a diminished pressure, and the operation repeated until no change takes place. The cup is now filled with water, j opened, and the reagent completely washed out into an ordinary tumbler placed beneath the burette. Four times filling of F should be sufficient for this purpose. The cup is now filled to the 25-cc. mark, j opened, and the reading taken as before.

The difference between this reading and the initial represents the number of cubic centimeters of carbon

dioxide; this divided by the volume of the gas taken gives the per cent of this constituent.

Determination of Oxygen.—The water is again sucked out, and potassium pyrogallate solution introduced, similarly to potassium hydrate; this is displaced by water, and the reading taken as before. The difference between this and the last reading is the volume of oxygen present.

Determination of Carbonic Oxide.—The water is removed for a third time, and acid cuprous chloride solution introduced and the absorption made as before; this is washed out, first with water containing a little hydrochloric acid to dissolve the white cuprous chloride which is precipitated by the addition of water, and finally with pure water, and the reading taken as before. The difference between this and the preceding gives the volume of carbonic oxide present.

Notes.—Especial care should be taken not to grasp the burette by the bulb, as this warms the gas and renders the readings inaccurate. The stopcocks can conveniently be kept in the burette by elastic bands of suitable size. When the apparatus is put away for any considerable time, a piece of paper should be inserted between the key and socket of each stopcock to prevent the former from sticking fast. To ascertain when the absorption is complete, the burette is mounted in its clamp and allowed to drain until the meniscus is stationary, the dish containing the reagent raised until the tip is covered, *l* opened, and any change in level noted. If the meniscus rises, the absorption is incomplete and must be continued; if it remains stationary or falls, the absorption may be regarded as

finished.   In case the grease from the stopcocks
becomes troublesome inside the burette, it may be
removed by dissolving it in chloroform and washing
out with alcohol and then with water.   The object in
sucking the water not quite down to *l*, thus leaving a
little water in the burette, is to discover if *l* leaks, the
air rushing in causes bubbles.

The object in washing out each reagent and taking
all readings over water is to obviate corrections for
the tension of aqueous vapor over potassium hydrate,
hydrochloric acid, or any of the reagents which might
be employed.   The tension of aqueous vapor over
seven per cent caustic soda is less than over water.

Accuracy and Time Required.—The apparatus is
rather difficult to manipulate, but fairly rapid—about
twenty-five minutes being required for an analysis—
and accurate to one tenth of one per cent.

ELLIOTT APPARATUS.

Description.—The apparatus Fig. 10 consists of a
burette holding 100 cc. graduated in tenths of a cubic
centimeter and bulbed like the Bunte apparatus—the
bulb holding about 30 cc.; it is connected with a
levelling-bottle similar to the Orsat apparatus.   The
top of the burette ends in a capillary stopcock, the
stem of which is ground square to admit of close con-
nection with the "laboratory vessel," an ungraduated
tube similar to the burette, except of 125 cc. capacity.
The top of this "vessel" is also closed with a capil-
lary stopcock, carrying by a ground-glass joint a
thistle-tube *F*, for the introduction of the reagents.
The lower end of this " vessel " is closed by a rubber

stopper carrying a three-way cock *o*, and connected with a levelling-bottle *D*. The burette and vessel are held upon a block of wood—supported by a ring stand—by fine copper wire tightened by violin keys.

Manipulation.—The ground-glass joints are lubricated as in the Bunte apparatus. The levelling bottles are filled with water, the stopcocks opened, and the bottles raised until the water flows through the stopcocks *m* and *n*. *m* is connected with the source whence the gas to be analyzed is to be taken, *n* closed, *D* lowered and rather more than 100 cc. drawn in, and *m* closed. *n* is opened, *D* raised and *E* lowered, nearly 100 cc. of gas introduced, and *n* closed; by opening *m* and raising *D* the remainder of the gas is allowed to escape, the tubes being filled with water and *m* closed. *n* is opened and the water brought to the reference-mark; the burette is allowed to drain one minute, the level of the water in *E* is brought to the same level as in the burette, and the reading taken.
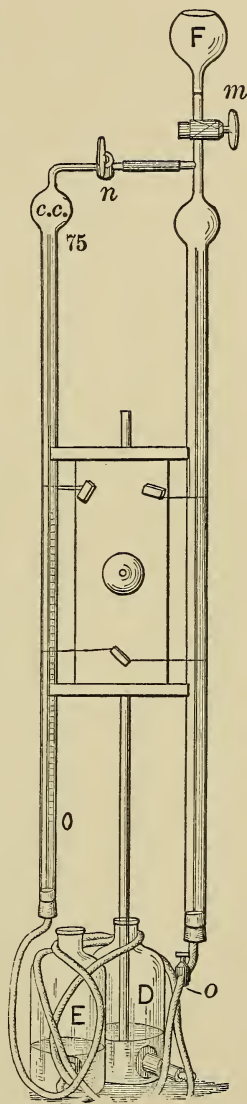
FIG. 10.—ELLIOTT GAS APPARATUS.

Determination of Carbon Dioxide.—By raising *E*, opening *n*, and lowering *D*, the gas is passed over into the laboratory vessel; *F* is filled within half an inch

of the top with potassium hydrate, *o* closed, *m* opened, and the reagent allowed to slowly trickle in. A No. 3 evaporating-dish is placed under *o*, and this turned to allow the liquid in the laboratory vessel to run into the dish. At first this is mainly water, and may be thrown away; later it becomes diluted reagent and may be returned to the thistle-tube. When the depth of the reagent in the thistle-tube has lowered to half an inch, it should be refilled either with fresh or the diluted reagent and allowed to run in until the absorption is judged to be complete, and the gas passed back into the burette for measurement. To this end close *o* and then *m*, raise *E*, open *n*, and force some pure water into the laboratory vessel, thus rinsing out the capillary tube. Now raise *D* and lower *E*, shutting *n* when the liquid has arrived at the reference-mark. The burette is allowed to drain a minute, the level of the water in the bottle *E* brought to the same level as the water in the burette, and the reading taken.

Determination of Oxygen.—The manipulation is the same as in the preceding determination, potassium pyrogallate being substituted for potassium hydrate; the apparatus requiring no washing out.

Determination of Carbonic Oxide.—The laboratory vessel, thistle-tube, and bottle if necessary, are washed free from potassium pyrogallate and the absorption made with acid cuprous chloride similarly to the determination of carbon dioxide. The white precipitate of cuprous chloride may be dissolved by hydrochloric acid.

Accuracy and Time Required.—The apparatus is as accurate for absorptions as that of Orsat; it is stated to be much more rapid—a claim which the writer cannot substantiate. It is not as portable, is more fragile, and more troublesome to manipulate, and as the burette is not jacketed it is liable to be affected by changes of temperature.

Notes.—In case at any time it is desired to stop the influx of reagent, *o* should be closed first and then *m*; the reason being that the absorption may be so rapid as to suck air in through *o*, *m* being closed.

The stopcock should be so adjusted as to cause the reagent to spread itself as completely as possible over the sides of the burette.

By the addition of an explosion-tube it is used for the analysis of illuminating-gas,* bromine being used to absorb the " illuminants." Winkler † has shown that this absorption is incomplete, and Hempel ‡ that explosions of hydrocarbons made over water are inaccurate, so that the apparatus can be depended upon to give results upon methane and hydrogen only within about two per cent.

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* Mackintosh, Am. Chem. Jour. **9**, 294.

† Zeitsch. f. Anal. Chem. **28**, 286.

‡ Gasanalytische Methoden, p. 102.

CHAPTER III.

MEASUREMENT OF TEMPERATURE.

In the majority of cases, the ordinary mercurial thermometer will serve to determine the temperature of the chimney-gases. It should not be inserted naked into the flue, but be protected by a bath of cylinder, or raw linseed oil, contained in a brass or iron tube. These tubes may be half an inch inside diameter and two to three feet in length. Temperatures as high as 625° C. have been observed in chimneys; this lasts of course but for a moment, but would be sufficient to burst the unprotected thermometer.

For the observation of higher temperatures, recourse must be had to the " high-temperature thermometers," filled with carbon dioxide under a pressure of about one hundred pounds, giving readings to 550° C.* These may be obtained of the dealers in chemical apparatus; some require no bath, being provided with a mercury-bath carefully contained in a steel tube, and the whole enclosed in a bronze tube.†

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* Those made by W. Apel, Göttingen, Germany, are about three feet long, the scale occupying about one foot, thus avoiding the necessity of withdrawing the thermometer from the bath for reading.

† Those made by the Hohmann and Maurer Co., Brooklyn, N. Y.

These thermometers should be tested from time to time either by comparison with a standard or by insertion in various baths of a definite temperature. Some of the substances used for these baths are: water, boiling-point 100°; naphthalene, Bpt. 219°; benzophenon, Bpt. 306°; and sulphur,* Bpt. 445°. Care should be taken that the bulb of the thermometer does not dip into the melted substance, but only into the vapor, and that the stem exposure be as nearly as possible that in actual use.

For the measurement of temperatures beyond the range of these thermometers the Le Chatelier thermo-electric pyrometer may be used. This consists of a couple formed by the junction of a platinum and platinum-10% rhodium wire, passing through fire-clay tubes in a porcelain or iron envelope and connected with a galvanometer. The hotter the junction is heated the greater the current and the galvanometer deflection; this latter is determined for several points, naphthalene, sulphur, and copper, Mpt. 1095° C., or even platinum, 1760° C., and a plot made with galvanometer-readings as abscissæ and temperatures as ordinates. From this the temperature corresponding to any deflection is readily obtained.

The exact description of the instrument and details of calibration are, however, beyond the scope of this work, and the student is referred for these to articles by Le Chatelier, Société Technique de l'Industrie du Gaz, 1890, abstracted in Jour. Soc. Chem. Industry,

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* In testing the H. & M. thermometers in sulphur-vapor, the bronze tube should be prevented from corrosion by the vapor by a glass envelope.

9, 326, and Holman, Proc. Am. Academy, 1895, p. 234.

An error of 5° in the reading of the thermometer affects the final result by about 20 calories.

In case neither of these methods be available nor
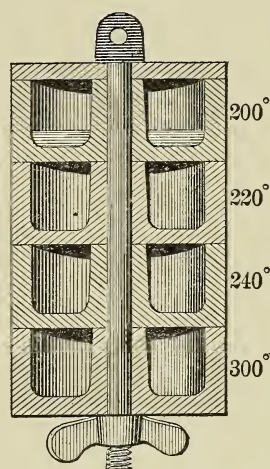
FIG. 11.—MELTING-POINT BOXES.

applicable, use may be made of the melting-points of certain metals or salts contained in small cast-iron boxes, Fig. 11.   The melting-points of certain metals and salts are given in Table VII.

CHAPTER IV.

CALCULATIONS.

As has been already stated in the Introduction, the object of analyzing the flue-gases is to ascertain, first, the completeness of the combustion, especially the amount of air which has been used or the "pounds of air per pound of coal," and second, the amount of heat passing up chimney.

1. To Ascertain the Number of Pounds of Air per Pound of Coal.—A furnace-gas gives 11.5% CO_2, 7.4% O, 0.9% CO, and 80.2% N. Data: atomic weights, $O = 16$, $C = 12$; weight liter $CO_2 = 1.966$ grs., of O, 1.43 grs., of CO, 1.251 grs. Find the number of grams of each constituent in 100 liters of the furnace-gas, and from this the weight of carbon and weight of oxygen. 11.5 (liters CO_2) $\times 1.97$ (wt. liter CO_2) = 22.66 grms. CO_2; now $\frac{32}{44}\left(\frac{O_2}{CO_2}\right)$ of this is oxygen = 16.41 grms., 6.25 grms. is carbon. The weight of free oxygen is $7.4 \times 1.43 = 10.58$ grms. The weight of carbon and oxygen in the carbonic oxide is $0.9 \times 1.25 = 1.12$ grms. CO. Now $\frac{16}{28}\left(\frac{O}{CO}\right)$ is oxygen or 0.64 grm., and 0.48 grm. is carbon. There are then present in 100 liters of the gas 27.63 grms. oxygen and 6.73 grms. carbon; corresponding to 119.6 grms. air

to 6.73 grms. carbon, air being 23.1% oxygen by weight; or 17.77 $\left.\begin{array}{l}\text{grms.}\\\text{lbs.}\end{array}\right\}$ air per $\left.\begin{array}{l}\text{grm.}\\\text{lb.}\end{array}\right\}$ *carbon.* If the coal be 83% carbon, this figure must be diminished accordingly, giving in this case 14.75 lbs. air per lb. of *coal.* Theory requires 11.54 lbs. air per lb. of carbon, but in practice the best results are obtained by increasing this from 50% to 100%.[*]

2. To Ascertain the Quantity of Heat Passing up Chimney.—Determine the volume of gas generated from one kilo of coal when burned so as to produce the gas the analysis of which has just been made according to the directions given. The chemical analysis of the coal is as follows: moisture 1.5%, sulphur 1.2%, carbon 83%, hydrogen 2.5%, ash 11.4%, oxygen and nitrogen (by difference) 0.4%. Then there are in one kilo of coal 830 grms. carbon, of this suppose but 800 to be burned, the remaining 30 grms. going into the ash; of the 800 grms. 625/673 or 743 grms. produced carbon dioxide, and 48/673 or 57 grms. produced carbonic oxide. From 6.25 grms. carbon were produced 11.5 liters carbon dioxide in the problem in 1; hence 743 grms. would furnish 1367 liters. $6.25 : 743 :: 11.5 : y.$ $y = 1367.$ Similarly 57 grms. carbon would furnish 107.4 liters carbonic oxide. $0.48 : 57 :: 1.12 : z.$ $z = 107.4.$ The volume of oxygen can be found by the proportion 11.5 (% CO_2) : 7.4 (%O) :: 1367 : $x.$ $x = 880$ liters. In the same manner the nitrogen is found to be 9535 liters. $11.5 : 80.2 :: 1367 : u.$ $u = 9535.$ One kilo of coal under these conditions furnishes 1.367 cu. meter

carbon dioxide, 0.107 c. m. carbonic oxide, 0.880 c. m. oxygen, and 9.535 c. m. nitrogen.

The quantity of heat carried off by each gas is its rise of temperature × its weight × its specific heat. The specific heats of the various gases are shown in the table below, and for facility in calculation, a column is given obtained by multiplying the weight by the specific heat; multiplying the volumes obtained in the previous calculation by the numbers in this column and by the rise in temperature gives the number of calories (C) that each gas carries away.

TABLE OF SPECIFIC HEATS OF VARIOUS GASES.[*]

Name of Gas.	Sp. Heat.	Wt. of Cu. M. Kg.	Sp. Heat × Wt. of Cu. M.	Log.
Carbon dioxide (10°–350°).	0.234	1.98	0.463	9.6656
" monoxide.........	0.245	1.26	0.308	9.4886
Oxygen.................	0.217	1.43	0.311	9.4928
Nitrogen...............	0.244	1.26	0.306	9.4857
Aqueous vapor..........	0.480	0.80	0.387	9.5877

In the test the average temperature of the escaping gases was 275° C.; that of the air entering the grate was 25° C., a rise of temperature of 250° C. As shown by the wet-and-dry-bulb thermometer, the air was 50 per cent saturated with moisture.

The calculation of the heat carried away is then for:

	Cu. M.					C.
Carbon dioxide..........	1.367	× 250	× 0.463	=	158.2
Carbonic oxide..........	0.107	× "	× 0.308	=	8.2
Oxygen.................	0.880	× "	× 0 311	=	68.4
Nitrogen...............	9.535	× "	× 0.306	=	729.3
Total.............	11.989				964.1

[*] Fischer, Tech. d. Brennstoffe, p. 267.

There is, however, another gas passing up chimney of which we have taken no cognizance, namely, water-vapor; this comes from the moisture in the coal, from the combustion of hydrogen in the coal, and from the air entering the grate; its volume is calculated as follows:

The moisture in the coal as found by chemical analysis was $1.5\% = 0.015$ kg.; the hydrogen in the coal was $2.5\% = 0.025$ kg. The amount of water this forms when burned is nine times its weight, 0.025 kg. $\times 9 = 0.225$ kg. The moisture in the air entering the grate would be, if completely saturated, 22.9 grams per cubic meter, as shown by Table I; it was, however, but 50% saturated. The quantity is then, the volume of air used per kilogram of coal $\times$ moisture contained in it, or $11.989 \times 22.9 \times 0.50 = 0.137$ kg. The weight of aqueous vapor passing up chimney per kilogram of coal is $0.015 + 0.225 + 0.137 = 0.377$ kg.; the quantity of heat that this carries off is $0.377 \times 250 \times 0.480 = 45.2$ C. The total quantity of heat passing up chimney is then 1009.3 C. The heat of combustion of this coal as found by Mahler's calorimetric bomb was 7220 C.; hence the percentage of heat carried off is $1009/7220 = 14\%$.

The preceding calculations though correct are tedious, so much so, as to almost preclude their use for an hourly observation of the firing. They should be employed, however, in making the final calculation of a boiler-test, using the averages obtained.

In rapid work the following formula will be found more applicable: Let **o** and **n** represent the percentages of oxygen and nitrogen found in the chimney-

gas; then the ratio of the air actually used to that theoretically necessary is expressed by the formula

$$\frac{21}{21 - \left(\dfrac{79 \text{ o}}{\text{n.}}\right)}.$$

Applying it in the case of the flue-gas given, it becomes

$$\frac{21}{21 - \left(\dfrac{79 \times 7.4}{80.2}\right)} = \frac{21}{13.7} = 1.533 \text{ ratio.}$$

Multiplying this by 11.54, the theoretical number of pounds of air per pound of carbon, we obtain 17.69 as against 17.77 on page 28.

Lunge[*] has given a shorter method for the determination of the quantity of heat passing up chimney, and one which does not involve the analysis of the coal.

One kilogram of pure carbon yields, when burned, 1.854 cubic meters of carbon dioxide under standard conditions and evolves 8080 calories. By the analysis of the gases we obtain the percentages of carbon dioxide, oxygen, and nitrogen. Let $k =$ per cent of carbon dioxide, then $100 - k$ represents the per cent of nitrogen and oxygen together. Let 1.854 cu. m. represent this per cent of carbon dioxide, then x, the volume of the nitrogen and oxygen, may be found by the proportion $1.854 : k :: x : (100 - k)$.

$$\therefore \quad x = 1.854 \frac{(100 - k)}{k}.$$

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[*] Zeit. f. angewandte Chemie, 1889, 240.

Let t be the temperature of the air entering the grate, and t' that of the gases in the chimney; then $t' - t$ represents the rise of temperature. Let c represent the specific heat of a cubic meter of carbon dioxide $= 0.46$, p. 29, and c' that of a cubic meter of nitrogen $= 0.31$. Then the loss of heat is represented by the formula

$$1.854\,(t' - t)c + 1.854\left(\frac{100 - k}{k}\right)(t' - t)c'.$$

The percentage of heat lost is then

$$\frac{\text{Loss of heat} \times 100}{8080}.$$

Substituting in this formula for k, 11.5, $t' - t$, $250°$, we obtain

Loss of heat $=$

$$(1.854)(250)(.46) + 1.854\left(\frac{88.5}{11.5}\right)(250)(0.31) = 1319.$$

$$\frac{1319 \times 100}{8080} = 16.3\%,$$

loss of heat as against 14% on page 30.

This formula gives results which are usually 2 to $2\frac{1}{2}$ per cent too high.

Determination of Loss Due to Formation of Carbonic Oxide.—On page 28 we see that 57 grams of carbon burned to carbonic oxide; for every gram of carbon burned to carbonic oxide there is a loss of 5.66 C., in this case a loss of 323 C. The heating value of the coal is 7220 C., hence the loss is 4.5 per cent.

Determination of the Loss Due to Unconsumed Fuel.—The per cent of carbon in the ash being determined by chemical analysis, and the weight of the ash being known, the weight of the unburned carbon can be determined. This can be then calculated as coal, which divided by the weight of coal fired gives the loss due to this source. This loss varies from 5 to 7 per cent. This should be taken cognizance of in calculating the volume of flue-gases formed from one kilogram of coal.

CHAPTER V.

REAGENTS AND ARRANGEMENT OF THE LABORATORY.

THE reagents used in gas-analysis are comparatively few and easily prepared.

Hydrochloric Acid, Sp. gr. 1.10.—Dilute "muriatic acid" with an equal volume of water. In addition to its use for preparing cuprous chloride, it finds employment in neutralizing the caustic solutions which are unavoidably more or less spilled during their use.

Acid Cuprous Chloride.—The directions given in the various text-books being troublesome to execute, the following method, which is simpler, has been found to give equally good results. Cover the bottom of a two-liter bottle with a layer of copper oxide or " scale " ⅜ in. deep, place in the bottle a number of pieces of rather stout copper wire reaching *from top to bottom*, sufficient to make a bundle an inch in diameter, and fill the bottle with common hydrochloric acid of 1.10 sp. gr. The bottle is occasionally shaken, and when the solution is colorless, or nearly so, it is poured into the half-liter reagent bottles, containing copper wire, ready for use. The space left in the stock bottle should be immediately filled with hydrochloric acid (1.10 sp. gr.).

By thus adding acid or copper wire and copper oxide when either is exhausted, a constant supply of this reagent may be kept on hand.

The absorption capacity of the reagent per cc. is, according to Winkler, 15 cc. CO; according to Hempel 4 cc. The author's experience with Orsat's apparatus gave 1 cc.

Care should be taken that the copper wire does not become entirely dissolved and that it extend from the top to the bottom of the bottle; furthermore the stopper should be kept thoroughly greased the more effectually to keep out the air, which turns the solution brown and weakens it.

Ammoniacal Cuprous Chloride. — The acid cuprous chloride is treated with ammonia until a faint odor of ammonia is perceptible; copper wire should be kept in it similarly to the acid solution. This alkaline solution has the advantage that it can be used when traces of hydrochloric acid vapors might be harmful to the subsequent determinations, as, for example, in the determination of hydrogen by absorption with palladium. It has the further advantage of not soiling mercury as does the acid reagent.

Absorption capacity, 1 cc. absorbs 1 cc. CO.

Cuprous chloride is at best a poor reagent for the absorption of carbonic oxide; to obtain the greatest accuracy where the reagent has been much used, the gas should be passed into a fresh pipette for final absorption, and the operation continued until two consecutive readings agree exactly. The compound formed by the absorption—possibly Cu_2COCl_2—is very unstable, as carbonic oxide may be freed from the

solution by boiling or placing it in vacuo; even if it be shaken up with air, the gas is given off, as shown by the increase in volume and subsequent diminution when shaken with fresh cuprous chloride.

Potassium Hydrate.—(*a*) For carbon dioxide determination, 500 grams of the commercial hydrate is dissolved in 1 liter of water.

Absorption capacity, 1 cc. absorbs 40 cc. CO_2.

(*b*) For the preparation of potassium pyrogallate for special work, 120 grams of the commercial hydrate is dissolved in 100 cc. of water.

Potassium Pyrogallate.—Except for use with the Orsat or Hempel apparatus, this solution should be prepared only when wanted. The most convenient method is to weigh out 5 grams of the solid acid upon a paper, pour it into a funnel inserted in the reagent bottle, and pour upon it 100 cc. of potassium hydrate (*a*) or (*b*). The acid dissolves at once, and the solution is ready for use.

If the percentage of oxygen in the mixture does not exceed 28, solution (*a*) may be used;* if this amount be exceeded, (*b*) must be employed. Otherwise carbonic oxide may be given off even to the extent of 6 per cent.

Attention is called to the fact that the use of potassium hydrate purified by alcohol has given rise to erroneous results.

Absorption capacity, 1 cc. absorbs 2 cc. O.

Sodium Hydrate.—Dissolve the commercial hydrate in three times its weight of water. This may be

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* Clowes, Jour. Soc. Chem. Industry, **15**, 170.

employed in all cases where solution (*a*) of potassium hydrate is used. The chief advantage in its use is its cheapness, it costing but one tenth as much as potassium hydrate, a point to be considered where large classes are instructed. Sodium pyrogallate is, however, a trifle slower in action than the corresponding potassium salt.

ARRANGEMENT OF THE LABORATORY.

The room selected for a laboratory for gas-analysis should be well lighted, preferably from the north and east. To prevent changes in temperature it should be provided with double windows, and the method of heating should be that which will give as equable a temperature as possible. In the author's laboratory, instead of the usual tables, shelves are used, 18 inches wide and $1\frac{1}{4}$ inches thick, best of slate or soapstone, firmly fastened to the walls, 30 inches from the floor; the Orsat apparatus, when not in use, may be suspended from these. The reagents are contained in half-liter bottles fitted with rubber stoppers, placed upon a central table convenient to all. Here are found scales, funnels and graduates for use in making up reagents. Distilled water is piped around to each place by $\frac{1}{8}$-inch tin pipe and $\frac{3}{16}$-inch rubber tubing from a $\frac{1}{4}$-inch "main," being supplied at the temperature of the room from bottles placed about six feet above the laboratory shelves. A supply of a gallon per day per student should be provided.

At the right of each place is fixed a sand-glass of cylindrical rather than conical form, graduated to minutes for the draining of the burettes. The "egg-

timers '' found in kitchen-furnishing stores serve the purpose admirably.

'' Unknown gases '' for analysis are best contained in a Muencke double aspirator, Fig. 12, where they
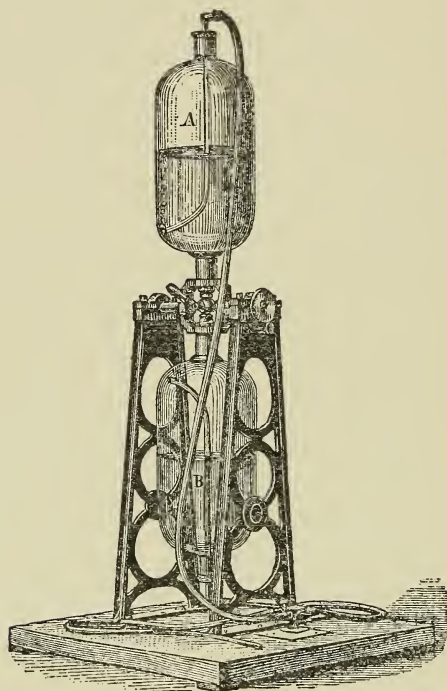
FIG. 12.—MUENCKE'S ASPIRATOR.

can be thoroughly mixed before distribution and conveyed by a pipe to the central table.

Finally, the laboratory should contain a stone-ware sink provided with an efficient trap of the same material, to prevent mercury from being carried into and corroding the lead waste-pipes.

Drawers should be provided with compartments for various sizes of rubber connectors, pinchcocks, glass tubing, stoppers and fittings, and tools. When working with the Orsat apparatus alone, three feet of shelf

space may be allowed to each student; when using this with another, as, for example, the Bunte, another foot should be added.

The course which the writer has been in the habit of giving to the Mechanical and Electrical Engineers embraces two exercises in the laboratory of two hours each, supplemented with four hours of lectures. The students in the laboratory make an analysis of air and an '' unknown '' furnace-gas, take and analyze an actual sample of chimney-gas, and make the calculation of heat lost and air used. In the lectures, the subject of gas-analysis and its other applications, and of fuels, their origin, description, preparation, analysis, and determination of heating value, are described.

CHAPTER VI.

FUELS—SOLID, LIQUID, AND GASEOUS: THEIR DERIVATION AND COMPOSITION.

The substances employed as fuels are:

a. Solid Fuels.—Wood, peat, brown, bituminous and anthracite coal, charcoal, coke, and oftentimes various waste products, as sawdust, bagasse, straw, and spent tan.

b. Liquid Fuels.—Crude petroleum and various tarry residues.

c. Gaseous Fuels.—Natural gas, generator, blast-furnace, water, and illuminating gas.

The essential constituents in all these are carbon and hydrogen; the accessory, oxygen, nitrogen, and ash; and the deleterious, water, sulphur, and phosphorus.

a. Solid Fuels.

Wood is composed of three substances—*cellulose,* or woody fibre $(C_6H_{10}O_6)_n$; *the components of the sap,* the chief of which is lignine, a resinous substance of identical formula with cellulose; and *water.* The formation of cellulose from carbon dioxide and water may be represented by the equation

$$6CO_2 + 5H_2O = C_6H_{10}O_6 + 6O_2.$$
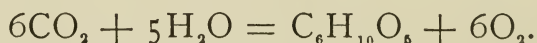
The amount of water which wood contains determines its value as a fuel. This varies from 29 per cent in ash

to 50 per cent in poplar; it varies also with the season at which the wood is cut, being least when the sap is in the roots—in December and January. This difference may amount to 10 per cent in the same kind of wood.

The harder varieties of wood make the best fuel, a cord of seasoned hardwood being about equal to a ton of coal. Yellow pine, however, has but half this value; the usual allowance in a boiler-test is 0.4 the value of an equal weight of coal.

The ash of wood is mainly potassium carbonate, with traces of other commonly occurring substances, as lime, magnesia, iron, silica, and phosphoric acid.

The *percentage composition of wood* may be considered as approximately,

Water.	Carbon.	Hydrogen.	Oxygen.	Ash.	Sp. Gr.
20	39	4.4	35.6	1	0.5.*

When burned it yields about 4000 C. per kilo, and requires 6 times its weight of air or 9.22 cu. m. (148 cu. ft. per pound) for its combustion.

Peat, though finding considerable application in Europe, is but little used in this country. It is produced by the slow decay under water of certain swamp plants, more especially the mosses (Sphagnaceæ), evolving methane (CH_4) (marsh-gas) and carbon dioxide (CO_2).

It contains considerable moisture, from 20 to 50 per cent, and 10 per cent even when "thoroughly dry." Thirty per cent of its available heat is employed in evaporating this moisture. The high content of ash, from 3 to 30 per cent, averaging 15 per cent, also diminishes its value as a fuel.

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* Mills & Rowan, Fuels, p. 11.

The ash of peat differs from that of wood in containing little or no potassium carbonate.

The *percentage composition of peat* may be considered as approximately,

Water.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Ash.	Sp. Gr.
16.4	41.0	4.32	3.8	2.6	11.9	1.05.

Such peat is about equivalent to wood in its heating effect, one pound evaporating from 4.5 to 5 pounds of water.

Coal.—Geologists tell us that coal was probably produced by the decay under fresh water of plants belonging principally to the Conifer, Fern and Palm families; these flourished during the Carboniferous Age to an extent which they never approached before or since. Representatives of the last family, which it is thought produced most of the coal, have been found 2 to 4 feet in diameter and 80 feet in height.

By their decay, carbon dioxide '' choke-damp,'' marsh-gas '' fire-damp,'' and water were evolved. The change might be represented by the equation

$$6C_6H_{10}O_5 = 7CO_2 + 3CH_4 + 14H_2O + C_{26}H_{20}O_2.$$

Cellulose.   Bituminous Coal.

Some idea of the density of the vegetation and the time required may be obtained from the fact that it has been calculated that 100 tons of vegetable matter —the amount produced per acre per century—if compressed to the specific gravity of coal and spread over an acre would give a layer less than 0.6 of an inch thick. Now four fifths of this is lost in the evolution of the gaseous products, giving as a result an accumu-

lation of *one eighth of an inch per century*, or one foot in 10,000 years.*

Brown Coal or Lignite may be regarded as forming the link between wood and coal; geologically speaking it is of later date than the true coal. Most of the coal west of the Rocky Mountains is of this variety.

As its name denotes, it generally is of brown color —although the western coal is black—and has a conchoidal fracture. It contains a large quantity of water when first mined, as much as 60 per cent, and when " air-dry " from 15 to 20 per cent. The per cent of ash is also high, from 1 to 20 per cent.

·The *percentage composition of brown coal* may be considered as approximately,

Water.	Carbon.	Hydrogen.	Oxygen and Nitrogen.	Ash.	Sp. Gr.
18.0	50.9	4.6	16.3	10.2	1.3.

Bituminous Coal.—This is the variety from which all the following coals are supposed to have been formed, by a process of natural distillation combined with pressure. According to the completeness of this process we have specimens which contain widely differing quantities of volatile matter. This forms the true basis for the distinguishing of the varieties of coal. In ordinary bituminous coal this volatile matter amounts to 30 or 40 per cent. Three varieties of bituminous coal are ordinarily distinguished, as follows:

Dry or non-caking—those which burn freely with but little smoke and—as the name denotes—do not cake

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* In case the student desires to follow in a more extended manner the geology of coal, reference may be had to Le Conte's " Elements of Geology," pp. 345–414 3d ed.

together when burned.   The coals from Wyoming are an example of this class.

Caking—those which produce some smoke and cake or sinter together in the furnace.   An example of these is the New River coal.

Fat or Long-flaming—those producing much flame and smoke and do or do not cake in burning; volatile matter 50 per cent or more.   Some of the Nova Scotia coals belong to this class.

Bituminous coal varies much in its composition—is black or brownish black, soft, friable, lustrous, and of specific gravity of 1.25 to 1.5.

Moisture varies from 0.25 to 8 per cent, averaging about 5.

The *percentage composition of bituminous coal* may be considered as approximately,*

Water.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Ash.	Sulphur.
0.6	80.5	4.9	5.4	2.1	5.8	0.7.

Semi-Bituminous or Semi-Anthracite Coal is upon the border-line between the preceding and the following variety; it is harder than bituminous, contains less volatile matter (15 to 20 per cent), and burns with a shorter flame.   An example of this is the Pocahontas coal.

The *percentage composition of semi-bituminous and semi-anthracite coal* may be considered to be approximately,*

Water.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Ash.	Sulphur.
1.8	77.4	4.7	3.7	2.0	9.5	0.9.

Anthracite Coal is the hardest, most lustrous, and densest of all the varieties of coal, having a specific

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gravity of 1.3 to 1.75; it contains the most carbon and least hydrogen and volatile matter (5 to 10 per cent). It has a vitreous fracture and kindles with difficulty, burning with a feeble flame, giving little or no smoke and an intense fire. The Lehigh coal is an excellent example of this class.

The *percentage composition of anthracite coal* may be considered as approximately,*

Water.	Carbon.	Hydrogen.	Oxygen.	Nitrogen.	Ash.	Sulphur.
3.2	82.4	2.5	2.7	0.8	7.8	0.6.

The ash of coal varies from 1 to 20 per cent and is mainly clay—silicate of aluminium—with traces of lime, magnesia, and iron. When coal is burned it yields from 7500 to 8000 C. and requires about 12 times its weight of air, 18.44 cu. m. per kilo or 296 feet per pound. For the greatest economy Scheurer-Kestner † found that this should be increased from 50 to 100 per cent.

Charcoal is prepared by the distillation or smouldering of wood, either in retorts, where the valuable by-products are saved, or in heaps. It should be jet-black, of bright lustre and conchoidal fracture.

When wood is charred in heaps only about 20 per cent of its weight in charcoal is obtained—48 bushels per cord, or about half the percentage of carbon. When retorts or kilns are employed, the yield is increased to 30 per cent, and 40 per cent of pyroligneous acid of 10 per cent strength, with 4 per cent of tar, are obtained.

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* H. J. Williams.
† Jour. Soc. Chem. Industry, 7, 616.

The *percentage composition of wood-charcoal* may be considered as approximately,

Carbon.	Ash.	Sp. Gr.
97.0	3.0	0.2

Coke is prepared by the distillation of bituminous coal in ovens; these are of two types, those in which the distillation-products are allowed to escape—the " beehive " ovens—and those in which they are carefully saved, as the Otto-Hoffman, Semet Solvay, Simon-Carvés', and others.

From 63 to 65 per cent of the weight of the coal is obtained as coke in the " beehive " ovens, while in the Semet-Solvay 80 per cent is obtained, together with by-products, increasing the total value of the output nearly sevenfold. Good coke should possess a silvery lustre, a cellular structure, a metallic ring, contain practically no impurities, and be capable of bearing a heavy burden in the furnace.

The analysis of Connellsville coke with the coal from which it is prepared is given below.

	Water.	Volatile Matter.	Carbon.	Sulphur.	Ash.
Coal	1.26	30.1	59.62	0.78	8.23
Coke	0.03	1.29	89.15	0.084	9.52

The Minor Solid Fuels.

Sawdust and **Spent Tan-bark** find occasional use, their value depending upon the quantity of moisture they contain. With 57 per cent of moisture 1 pound of tan-bark gave an evaporation of 4 pounds of water.

Wheat Straw finds application as fuel in agricultural districts, 3½ pounds being equal to 1 pound of coal. Upon sugar-plantations the crushed cane or **Bagasse**, partially dried, is extensively used as a

fuel. With 16 per cent of moisture an evaporation of 2 pounds of water per pound of fuel has been obtained.

b. Liquid Fuels.

These consist of petroleum and its products, and various tarry residues from processes of distillation, as from petroleum, coking-ovens, wood and shale. Liquid fuel possesses the advantage that it is easily manipulated, and the fire is of very equable temperature, very hot, and practically free from smoke.

Regarding the origin of petroleum, many theories have been proposed. That of Engler,* that it was formed by the distillation under pressure of animal fats and oils, the nitrogenous portions of the animals previously escaping as amines, seems most probable; it has yielded the best results of any hypothesis when tested upon an industrial scale.

Crude Petroleum varies greatly in color according to the locality; it is usually yellowish, greenish, or reddish brown, of benzine-like odor, and sp. gr. of 0.78 to 0.80. It " flashes " at the ordinary temperature; hence great care should be employed in its use and storage. Its *percentage composition* is shown below.

Carbon.	Hydrogen.
84.0–85.0	16.0–15.0

It is more than twice as efficient as the best anthracite coal. In practice 16 pounds of water per pound of petroleum have been evaporated, and an efficiency of 20,200 C. was obtained as against 8603 C. for anthracite.

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* Jour. Soc. Chem. Industry, 14, 648.

c. GASEOUS FUELS.

Natural Gas is usually obtained when boring for petroleum and consists mainly of methane and hydrogen, although the percentage varies with the locality. The Findlay, Ohio,* gas is of the following composition:

CH_4	H	N	O	C_2H_4	CO_2	CO	H_2S	Sp. Gr.
92.6	2.3	3.5	0.3	0.3	0.3	0.5	0.2	0.57

Blast-furnace, Producer, or Generator Gas is the waste gas issuing from the top of a blast-furnace or obtained by partially burning coal by a current of air in a special furnace—a gas-producer or generator. It is mainly carbonic oxide and nitrogen.

	CO	N	CO_2	H	CH_4	Sp. Gr.
Blast-furnace gas	34.3	63.7	0.6	1.4		
Producer gas	23.5	65.	1.5	6.0	3.0	1.0

Fischer † states that 1 kg. coal gives 4.5 cu. m. gas of 4760 C., the coal giving 7950 C. or about 60 per cent of the value of the coal. This is calculated on the heating effect of the cold gas; if it were used hot as it leaves the producer, at about 690° C., the heating effect would be increased by 850 C.

Water-gas.—If, instead of passing simply air over hot coal, water-vapor be employed, it is decomposed, giving carbonic oxide and hydrogen, according to the equation $H_2O + C = CO + H_2$, and the resulting mixture is called water-gas. Its *percentage composition* is as follows:

CO	H	CH_4	CO_2	N	O	Sp Gr.
45.8	45.7	2.0	4.0	2.0	0.5	0.57

* Orton, Geology of Ohio, vol. VI. p. 137.
† Wagner's Chemical Technology.

Fischer * states that 1 kg. coal gives about 1.2 cu. m. gas, or about 58 per cent of the heating value.

Coal or Illuminating Gas was formerly produced by the distillation of bituminous coal; it is at present largely made by the enriching of water-gas. "Gas-oil," a crude naphtha, is blown into the water-gas generator and changed to a permanent gas by the heat. Coal-gas is of the following composition:

H	CH$_4$	CO	C$_2$H$_4$	CO$_2$	N	O	Sp. Gr.
47.0	40.5	6.0	4.0	0.5	1.5	0.5	0.4

1 kilo of coal gives about 0.3 cubic meter of gas, or about 20 per cent of the heating value.

Heating Value of these Gases.

Prof. Orton † gives the following relative values of the various gases. Omitting in all cases losses by radiation and assuming that the gases escape at 500° F. and are burned with 20 per cent excess of air, 1000 cu. ft. of each gas would evaporate from 60° F. to 212° F. the following quantities of water expressed in pounds:

Natural gas 893
Coal   "   591
Water   "   262
Producer "   115

Natural gas requires for its combustion about eleven times its volume of air, allowing for 20 per cent excess.

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* Taschenbuch für Feuerungs Techniker, p. 27.
† Ohio Geology, vol. VI. p. 544.

CHAPTER VII.

METHODS OF ANALYSIS AND DETERMINATION OF THE HEATING VALUE OF FUEL.

SAMPLING.

A FEW representative lumps or shovelfuls are taken from each barrow or from various points in the pile, and the whole spread out in a low circular heap. Diameters are drawn at right angles in it and opposite quarters taken, these mixed and treated similarly to the whole sample. The operation is continued until a sample of a few pounds is obtained. This is roughly crushed and samples taken at different points for the moisture determination; it is then further quartered down until a sample of 200 grams which passes a 60-mesh sieve is obtained.

The methods employed in the analysis of fuels are largely a matter of convention, various methods giving varied results; for example, it is well-nigh impossible to obtain accurately the percentage of moisture in coal, as when heated sufficiently hot to expel the water some of the hydrocarbons are volatilized.

Moisture.—Dry from 1 to 2 grams of the sample in a watch-glass exactly one hour at 105° to 110° C.*

Coke and Volatile Matter.—Carry about one gram of the sample, weighed into a platinum crucible, to

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* See an article by Hale, Proc. Am. Soc. Mech. Eng. 1896.

the blast-lamp table; heat for *exactly* three and one half minutes by the watch in the hottest part of the Bunsen flame, it being from 7 to 8 inches long, and then for *exactly* three and one half minutes by the blast-lamp. The residue is *coke*. With anthracite coals the heating over the Bunsen burner is omitted.

Carbon and Hydrogen.—These are determined by burning the coal in a stream of air and finally in oxygen, the products of combustion, carbon dioxide and water, being absorbed in potassium hydrate and calcium chloride.

Apparatus Required.—Combustion-furnace similar to that shown in Fig. 13. Combustion-tube filled.
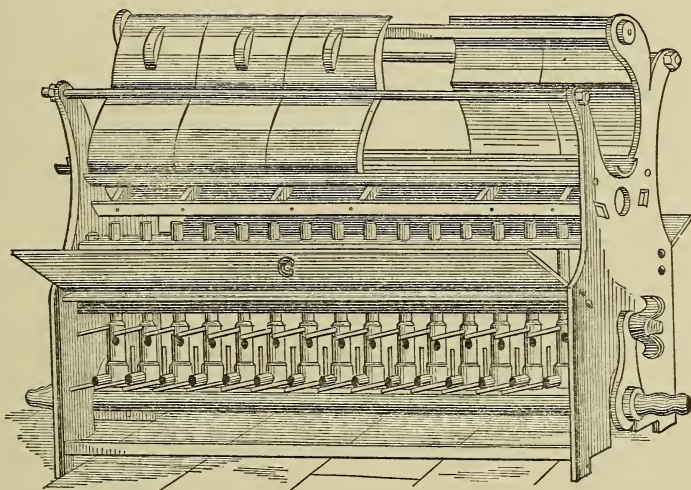

FIG. 13.—COMBUSTION-FURNACE.

Potash-bulbs with straight chloride of calcium tube filled. Chloride of calcium tube filled. Oxygen-holder, drying and purifying apparatus. Porcelain boat, desiccator, tongs, $\frac{1}{8}$-inch rubber tubing. Analytical balance.

The combustion-tube is of hard glass, $\frac{1}{2}$ inch in in-

ternal diameter and 36 inches long, closed with per-
forated rubber stoppers.   One end—called the front
end—is filled with a layer of copper oxide 12 inches
long, held in place by plugs of asbestos coming
within 4 inches of the stopper.   In coals rich in sul-
phur the oxide is partially replaced by a layer of
chromate of lead 2 inches long.   The position of the
boat containing the coal is immediately behind this
copper oxide; behind the boat is placed an oxidized
copper gauze roll, 6 inches long.   Before making the
combustion, the tube and contents should be heated
to a dull red heat in a stream of oxygen freed from
moisture and carbon dioxide by the purifying appa-
ratus, to burn any dust and dry the contents; it is
then ready for use.

The potash-bulbs are an aggregation of five bulbs,
the three lowest filled with potassium hydrate of 1.27
sp. gr., the other two serving as safety-bulbs, pre-
venting the liquid from being carried over into the
connectors.   They should be connected further with a
chloride of calcium tube to absorb any moisture carried
away by the dry gas.   When not in use they should
be closed with connectors carrying glass plugs.   Before
weighing they should stand at least fifteen minutes in
the balance-room to attain its temperature; the weight
should be to milligrams and without the connectors.

The chloride of calcium tube is of U form, provided
with bulbs for the condensation of the water; the
granular calcium chloride is kept in place by cotton
plugs, and the stopper neatly sealed in with sealing-
wax.   As calcium chloride may contain oxide which
would absorb the carbon dioxide formed, a current of

dry carbon dioxide should be passed through the tube and thoroughly swept out by dry air before use.

The chloride of calcium tube like the potash-bulbs should be placed in the balance-room fifteen minutes before weighing and, if the balance-case be dry, may be weighed without the connectors. It should be weighed to milligrams.

The oxygen-holder may be like the Muencke aspirator, Fig. 12. The oxygen should be purified by passing through potassium hydrate and over calcium chloride.

Operation.—The front stopper of the combustion-tube is slipped carefully upon the stem of the chloride of calcium tube and this connected to the potash-bulbs; 0 2 to 0.3 gram of the coal is carefully weighed into the porcelain boat (to 0.1 mg.), the roll removed, and the boat inserted behind the layer of copper oxide, and the roll and stopper replaced. The tube is now ready to be heated.

The front of the copper oxide is first heated, the heat being gradually extended back; at this time the rear end of the copper roll is heated and a slow current of purified air passed through. This method of gradual heating of the tube is followed until the layer of copper oxide and the rear portion of the roll are at a dull red heat. Heat is now cautiously applied to the coal and the current of air slackened. The volatile matter in the coal distils off, is carried into the layer of copper oxide and burned; the carbon dioxide formed can be seen to be absorbed by the potassium hydrate. When this absorption almost ceases, oxygen is turned on and the coal heated until

it glows.   The stream of oxygen should be so regulated as to produce but two bubbles of carbon dioxide in the bulbs per second.   If the evolution be faster, the gas is not absorbed.   When the coal has ceased glowing, oxygen is allowed to pass through the apparatus until a spark held at the exit of the last chloride of calcium tube (on the bulbs) re-inflames; the oxygen is allowed to run for fifteen minutes longer.   The current of oxygen is now replaced by purified air, and the heat moderated by turning down the burners and opening the fire-clay tiles; the air is allowed to run through for twenty minutes to thoroughly sweep out all traces of carbon dioxide and moisture.   The bulbs and U tube are disconnected, stopped up, allowed to stand in the balance-room, and weighed as before. The increase in weight in the bulbs represents the carbon dioxide formed; this multiplied by the factor 0.2727 gives the carbon.   Similarly the increase in the U tube, minus the water due to the moisture in the coal, represents the water formed, one ninth of which is hydrogen.

Notes.—At no time in the combustion should any water appear near the copper roll, as it is an indication that the products of combustion have gone backward into the purifying apparatus and hence are lost.   Such analyses should be repeated.   Should moisture appear in the front end, it may be *gently* heated to expel it. Both ends of the tube should be frequently touched with the hand during the combustion, and should be no hotter than may be comfortably borne, as the stoppers give off absorbable gases when highly heated. Care should be taken not to heat the tube too hot,

fusing the copper oxide into and spoiling it. One tube should serve for a dozen determinations.   It should not be placed upon the iron trough of the furnace, but upon asbestos-paper in the trough, to prevent fusion to the latter.

As will be seen, the execution of a combustion is not easy, and should only be intrusted to an experienced chemist.   The results obtained are usually 0.1 per cent too low for carbon and a similar amount too high for hydrogen.

Ash.—This is determined by weighing the residue left in the boat after combustion, or by completely burning one gram of the coal contained in a platinum dish ; often a stream of oxygen is used.

Nitrogen is determined by Kjeldahl's method, which consists in digesting the coal with strong sulphuric acid, aided by potassium permanganate, until nearly colorless.   The nitrogenous bodies are changed to ammonia, which forms ammonium sulphate and may be determined by rendering alkaline and distilling the solution.

Sulphur is determined by Eschka's method, consisting in heating for an hour one gram of the coal mixed with one gram of magnesium oxide and 0.5 grm. sodium carbonate in a platinum dish without stirring, using an alcohol-lamp, as gas contains sulphur. It is allowed to cool and rubbed up with one gram of ammonium nitrate and heated for 5 to 10 minutes longer.   The resulting mass is dissolved in 200 cc. of water evaporated to 150 cc., acidified with hydrochloric acid, filtered, and sulphuric acid determined in the filtrate in the usual way with barium chloride.

Oxygen is determined by difference, there being no direct method known.

The analysis of gaseous fuels is conducted upon the same principles as indicated in Chapter II, Hempel's apparatus being employed, for the use of which reference may be had to the author's '' Handbook of Gas Analysis.''

DETERMINATION OF CALORIFIC POWER OF SOLID AND LIQUID FUEL.

a. Direct Methods.

Many forms of apparatus have been proposed for this purpose; few, however, with the exception of those employing Berthelot's principle—of burning the substance under a high pressure of oxygen—have yielded satisfactory results. The apparatus of William Thomson,[*] and also that of Barrus, in which the coal is burnt in a bell-jar of oxygen, yield results varying as much as 8 per cent from the calculated value.[†] It is further inapplicable to semi-bituminous and anthracite coals, as the ash formed over the surface prevents the combustion of the coal beneath it.

Fischer's calorimeter [‡] is similar in principle, but is claimed to give very good results. [§]

Lewis Thompson's calorimeter, in which the coal is burnt in a bell-jar by the aid of oxygen furnished by the decomposition of potassium chlorate or nitrate, is

[*] Thomson, Jour. Soc. Chemical Industry, **5**, 581.

[†] Ibid., **8**, 525.

[‡] Zeit. f. angewandte Chemie, **12**, 351.

[§] Bunte, Jour. f. Gasbeleuchtung und Wasserversorgung, **34**, 21, 41.

open to several objections, the chief of which are: 1. The evolution of heat due to the decomposition of the oxidizing substance used. 2. Loss of heat due to moisture carried off by the gases in bubbling through the water. The results which it gives must be increased by 15 per cent.*

Hempel's apparatus † makes use of the Berthelot principle: the coal must be compressed into a cylinder for combustion—a process to which every coal is not adapted — only applicable to certain varieties of bituminous and brown coal. The mixture with the coal of any cementing or inflammable substance to form these cylinders carries with it the necessity of accurately determining its calorific power beforehand.

The best apparatus for the purpose is probably that of Mahler,‡ modified by Holman and Williams, the modifications consisting in replacing the enamel lining by electroplating the inside with gold and in improved methods of making the apparatus tight.

The Mahler apparatus, Fig. 15, consists of a mild-steel cylinder B, with walls half an inch thick, narrowed at the top for connection by a screw-joint with the cover carrying the vessel C to contain the coal. This cylinder or bomb is placed inside the calorimeter D, and this inside a jacket A. At the right is shown a portion of the oxygen-cylinder and the gauge.

For the following directions for its use the author is indebted to the kindness of Professor Silas W. Holman of the Institute of Technology.

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* Scheurer-Kestner Jour. Soc. Chemical Industry, **7**, 869.
† Hempel, '' Gasanalytische Methoden,'' p. 347.
‡ Mahler, Jour. Soc. Chemical Industry, **11**, 840.

Preparation of Bomb.—Remove the ring upon which it sits in the calorimeter.

Wash out the bomb. It need not be dry. Leave cover off.

See that the lead-ring washer *P*, Fig. 14, is in good condition. Unless its upper surface is fairly smooth the cover cannot be tightly closed. Repeated screwing on of the cover raises a burr of lead. When this becomes noticeable it must be removed by cutting with a knife-blade. If there is difficulty in making the cover tight, it is most likely to be due to this cause.
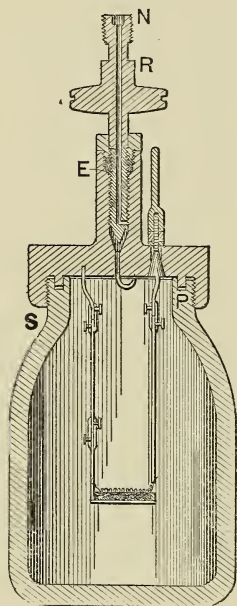
Grease the screw *S* upon the outside of the bomb slightly with tallow or a heavy oil, but be sure that none of the grease gets beyond the lead washer.

Fig. 14.—Mahler's Bomb.

Secure the bomb very firmly in the heavy clamp on the table.

Place the top on a ring or in a clamp of a lamp-stand and in an upright position.

Put in position the platinum tray *C* and the rod *E*, Fig. 15.

Twist on the loop of ignition-wire (fine platinum or iron). This must make good electrical contact with both *E* and the pan or its supporting rod. Failing this the current will not flow to fuse the wire. Failure to ignite is almost always traceable to this cause.

Pour into the tray a known weight of the substance

to be burned. If this be coal, slightly over one gram should be used. It is usually best inserted from a small test-tube weighed before and after, with due precautions against loss.

The ignition-wire should dip well into the coal.

The fineness required in the combustible depends

FIG. 15.—MAHLER'S APPARATUS COMPLETE.

upon its nature. Anthracite coal should be in a very fine powder. Trial will show whether any unburned grains remain, indicating that the combustible is too coarse.

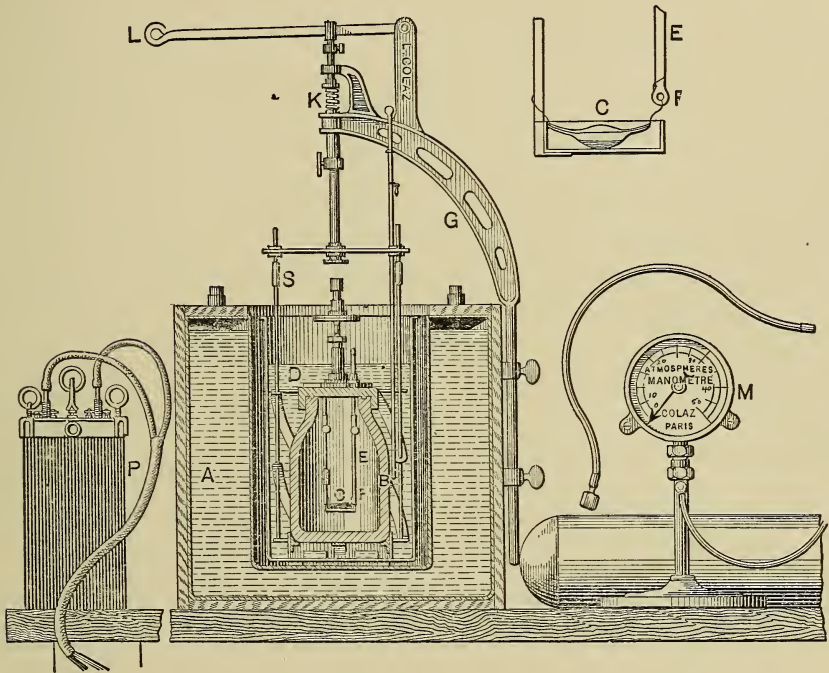The standard which carries the pressure-gauge should be screwed to the table near the bomb-clamp, and the oxygen cylinder must be placed near by so that the three may be easily connected by the flexible copper tube.

The top carrying the charge is then cautiously (to avoid loss of charge by jarring or draft) transferred to the bomb and screwed carefully home. The lifting is best done by hooking the fingers beneath the milled head at the top of the valve-screw R. The top must be set up hard by the wrench which takes the large nut cut on the cover. In setting this up it is desirable to use no more force than is necessary to secure a gas-tight bearing of the tongue of the cover against the lead washer P. Just the force required can only be learned by experience, but it is always considerable. A slight leak is unimportant, but it is not difficult to secure a tight seal if the lead washer be kept in good condition.

To fill with oxygen proceed as follows:

Screw down the valve-screw R *gently* to close the valve. Connect the copper tube to the oxygen-tank gauge, and to the bomb at N. See that there are leather washers at the joints. Turn the connecting nuts firmly but not violently home. The connections to the oxygen-tank and gauge are usually left undisturbed, and only that at N has to be made each time.

It is now necessary to test for leakage in the connections. To do this, as R is closed, it is only necessary to open the oxygen-tank *cautiously* by means of its wrench until the gauge indicates 5 or 10 atmospheres and then close it. As the tank when freshly charged has a pressure of 120 atmospheres, and the gauge reads only to 35 atmospheres, *care must be used in all manipulations not to overstrain the gauge*, also avoid suddenly releasing the pressure on the gauge. When this pressure is on, any leak in the connections

will be indicated by a drop in the gauge reading. If a leak exists, it must be removed or rendered extremely slow before proceeding further. It is most likely to be found in the joints, which must be tightened one by one until the leak stops.

Now to fill the bomb it is next necessary to open R. This could be done by merely turning back the milled head, or the nut just above it. But as this would put a twist into the copper connecting-tube (which many times repeated would break it), the better way is, holding one wrench in each hand, to loosen the connecting nut above N *by a half-turn*, holding R by the wrench and nut, then to turn the nut open a half-turn or until it is again tight in. This leaves the connections tight and R open into the bomb. The oxygen is then turned slowly on, and the bomb gradually fills. If a gram of coal is to be burned, a pressure of 25 atmospheres gives the proper amount of gas in the bomb. Note that the valve R and the inlet-tube have small borings. Thus the inflow of gas will be slow and the pressure in the connecting-tube will be higher than in the bomb. If, therefore, the tank be closed quickly, the gauge-reading will fall somewhat until these pressures equalize, and will then remain stationary unless there is a leak. The tank-cock must always be kept well under control to avoid overcharging either gauge or bomb.

When the bomb is full, close first the tank-cock. Then, to close R, put the wrenches on the nuts and, holding one from turning, set the other down until R is tight, *but not too tight*. Avoid straining R, which closes tight *very easily*. By this method the copper

tube is not twisted.   There is of course a slight leak
of gas from the bomb after N leaves the nut and
before R is closed, but the time required for the half-
turn is so short and the outflow so slow that the loss
is insignificant.   There is *no need to hurry* in this
operation.   Be deliberate and careful of the apparatus.
A valve like R is a nice piece of workmanship, and to
endure much usage it must be treated with care.

The bomb is now ready to be unclamped and set
into the ring preparatory to transfer to the calorimeter.
It can be left standing indefinitely, but must be
handled with caution (best by lifting with fingers
beneath R, to avoid spilling the charge).

Preparation of Calorimeter.—The outer jacket of
the calorimeter should be filled with water at about
the room temperature or a few degrees higher.   If
left standing from day to day it will usually be nearly
enough right.   It is well to stir it (blow air through
it) somewhat before beginning work, if it has stood for
some time.

Be sure that the inner surface of this jacket, i.e.,
the one which is next the calorimeter, is *thoroughly
dry*, and do not let any water spill into it—or remove
it if it does so.

Thoroughly dry the outer surface of the calorimeter
and *keep it so*.   Moisture depositing on or evaporating
from the surface of the calorimeter is sure to cause an
irregular error which may spoil otherwise good work.

Put the calorimeter in place.   Transfer the bomb to
it, and adjust the stirrer so that it works properly.

Pour in the proper amount of water, about 2.25

liters, at a suitable temperature, best by using marked flasks carefully calibrated beforehand.

Insert the thermometer.

See that the electrical attachments are ready for instantaneous use.   The whole is then ready for the combustion.

Combustion Observations.—With apparatus all in place run the stirrer briskly and continuously until the completion of the work.   Allow about five minutes for everything to come to a normal condition.   Then take temperature readings to at least 0.01° at each quarter minute for at least five minutes.   Record the times (h. m. s.) and corresponding thermometer-readings, thus:

Time.	Temp.	Remarks.
2^h 15^m 0^s	$15°.24$	After 5^m stirring
15	.24	
30	.25	
45	.25	
16 0	.25	
15	.26	
30	.26	
. . . .		
25 0	—	Coal ignited
15	15.6	
30	.9	
45	16.2	
26 0	.5	
etc.	etc.	

Exactly at the beginning of a noted minute close the electric circuit through the fuse-wire.   If the arrangements are right, this will cause the coal to ignite at once and the combustion is almost instantaneous.   Owing to the time required to transmit the

heat through the bomb to the water, the temperature, however, will continue to rise for two or three minutes. Keep up the steady stirring and the quarter-minute temperature-readings for at least ten minutes after ignition, recording as above. One or two observations may be unavoidably lost before and after ignition, but this does not materially affect the results. The readings during the rapid rise are also less close.

As soon as the rise begins to slow down, however, the hundredths of a degree must again be secured. This makes a series of observations of 15 to 20 minutes' duration. The use of the readings to obtain the cooling correction and the corrected rise of temperature of the calorimeter is given under the heading '' Cooling Correction '' farther on.

This completes the observations unless it is desired to test the character of the products of combustion. The bomb should now be opened and rinsed, as the nitric acid formed by the oxidation of the nitrogen in the coal and air attacks the metallic lining unless it be of gold. Also the top is more easily unscrewed at first than later. Leave the top off.

Before unscrewing the top of the bomb *be sure to open the valve R* to relieve the presure.

Heat Capacity of Bomb and Calorimeter.—The heat capacity of the bomb may be found:

1. From the weights and assumed specific heats of the parts.

2. By raising the bomb to an observed high temperature and immersing in water, i e., by the usual '' method of mixtures.''

3. By burning in it a substance of known heat of

combustion, such as pure naphthaline, and calculating back to find the heat capacity of the bomb.

The first method is not reliable. Errors of several per cent may enter in the assumed specific heats.

The second method is very difficult of exact performance, owing to the size and form of the bomb.

The third method is by far the most reliable, but of course depends on the correctness of the assumed heat of combustion of the substance used. That of naphthaline has been so well determined by Berthelot and others,* and the substance is so easily and cheaply obtained in a pure state, that dependence can be placed on the results. This method has the great advantage that it involves the use of the apparatus in precisely the same way as in subsequent determination, so that any systematic errors of method tend to cancel one another. It also determines at the same time the heat capacity of the calorimeter and stirrer just as used.

The capacity of the calorimeter and stirrer may best be determined in connection with that of the bomb by the third method just described. Otherwise it may be found by the first method, or by a method similar to the second, viz., by pouring into the calorimeter when partly full water of a known temperature different from that of the water in the calorimeter, noting all temperatures and weights. This last method, however, is very unsatisfactory in practice owing to the small heat capacity of the calorimeter and to the losses of heat in pouring the water, etc.

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* 1 gram of naphthaline evolves 9692 C. This is the average of 150 determinations by four different obervers.

A general expression for computing the heat of combustion from the bomb observations is as follows: Let n represent the number of grams of combustible, H the heat of combustion sought, W the weight of water in the calorimeter, and k the heat capacity, or water equivalent, of bomb, calorimeter, stirrer, thermometer, etc.; t_1 and t_2 represent the initial and final temperatures of the water. Then

$$nH = W(t_2 - t_1) + k(t_2 - t_1),$$

whence

$$H = \frac{1}{n}(W + k)(t_2 - t_1).$$

This expression is exact if t_2 is corrected for loss by cooling as described in the methods for "Cooling Correction," p. 67.

The value of k may be determined by either of the following methods; a simplification may, however, be introduced which will save much labor if an accuracy of not more than about one per cent is sought, provided that k is found by burning naphthaline or other known substance. Use enough of this substance to cause about the same rise, $t_2 - t_1$, (within 1°) as will be caused by one gram of coal. Omit the cooling correction entirely, using for t_2 the maximum temperature attained. Then compute k; this value will be erroneous by a small amount owing to the neglect of the correction. Now in subsequent measurements on coal also neglect the cooling correction, using for t_2 the maximum observed temperature as before, thus leaving an error in t_2. Since the rise $t_2 - t_1$ in both cases will be nearly the same, the error in k will almost

exactly affect that in t_2 in the coal-test, and the resulting value of H will be nearly free from this error. This method of course implies that W is nearly constant and that t_1 is systematically arranged to be either about at the air-temperature or a definite amount below it, as described under "Cooling Correction," so that the cooling loss is about the same. The time-interval from t_1 to t_2 must for the same reason be nearly constant in all cases.

Cooling Correction.—In all careful calorimetric work, one of the most troublesome sources of error is the loss or gain of heat by the calorimeter from its surroundings. This loss or gain is due to radiation, to air-convection currents, and to evaporation or condensation. Unavoidable irregularities in the conditions and the smallness of the quantities to be measured render the amount of the correction variable and its determination uncertain. Many methods of making the correction have been proposed. One of the best of these is the first of the two given below, but the second, although a little more troublesome in the execution of the work, appears to be more trustworthy in its results. The second method is to be used.

First Method.—This is described in the Physical Laboratory Notes, I, under "Specific Heat of Solids." In this method the water at the outset should be at such a temperature that it is gaining very slowly. For an open calorimeter this is about 1° or 2° below the air-temperature, but varies with circumstances. Water which has been long standing in the room is generally about right.

Second Method.—For the discussion and details

reference may be had to an article by Professor Holman in Proc. American Academy of Arts and Sciences, 1895, p. 245; also in The Technology Quarterly, **8**, 344.

Berthier's Method. — Another method of direct determination was proposed by Berthier in 1835.* It uses as a measure of the heating value the amount of lead which a fuel would reduce from the oxide; in other words, it is proportional to the amount of oxygen absorbed.

The method is as follows: Mix one gram of the fine dry coal with from 20 to 40 grams of oxychloride and oxide of lead, cover with 20 grams of oxide of lead (litharge), heat to redness in a crucible, and weigh the lead button formed. One part of carbon is equivalent to 34 parts of lead (or 235 calories C).

While this method of course can make no pretensions to scientific accuracy, yet the results seem as trustworthy as those obtained by calculation according to Dulong's formula (see *b*, below), and it is readily applicable.

b. Determination of Heating Value by Calculation.

The method of determination of the heating value first described, though exact, has the disadvantages that the apparatus is costly and the compressed oxygen is not easily obtained. To obviate these, it has been sought to obtain the heating value by calculation from the chemical analysis, the heating value of the constituents being known. This has the disadvantage that we have no absolute knowl-

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* Dingler's Polytechnisches Journal, **58**, 391.

edge—nay, not even an approximate idea—as to how the carbon, hydrogen, water, and sulphur exist in the coal, so that any formula must of necessity be quite removed from the truth. Dulong was the first to propose the method by calculation, and his formula is

$$H = \frac{8000c + 34500(h - \frac{1}{8}o)}{100},$$

c, h, and o representing the percentages of carbon, hydrogen, and oxygen in the coal.

Many modifications of this, considering the water formed, the heat of vaporization of carbon, or the volatile hydrocarbons, have been proposed.

Bunte [*] finds that the following formula gives results varying from + 2.8 to − 3.7 per cent:

$$\frac{8080c + 28800\left(h - \frac{o}{8}\right) + 2500s - 600w}{100}.$$

s and w represent the percentages of sulphur and water respectively. It is, however, inapplicable to anthracite coal. It would scarcely seem that the sulphur would be worth considering unless high, one per cent affecting the result but 0.3 per cent.

Mahler employs the formula

$$\frac{8140c + 34500h - 3000(o + n)}{100},$$

o and n representing oxygen and nitrogen, and states that it gives results within 3 per cent.

The results obtained by these formulæ for anthracite coal are as a rule considerably too low.

---

[*] Jour. für Gasbeleuchtung, **34**, 21–26 and 41–47.

CALORIFIC POWER OF GASEOUS FUEL.

a. Direct Determination.

Perhaps the best apparatus for the determination of the heating value of gases is the Junker calorimeter, Figs. 16 and 17. The following description is taken
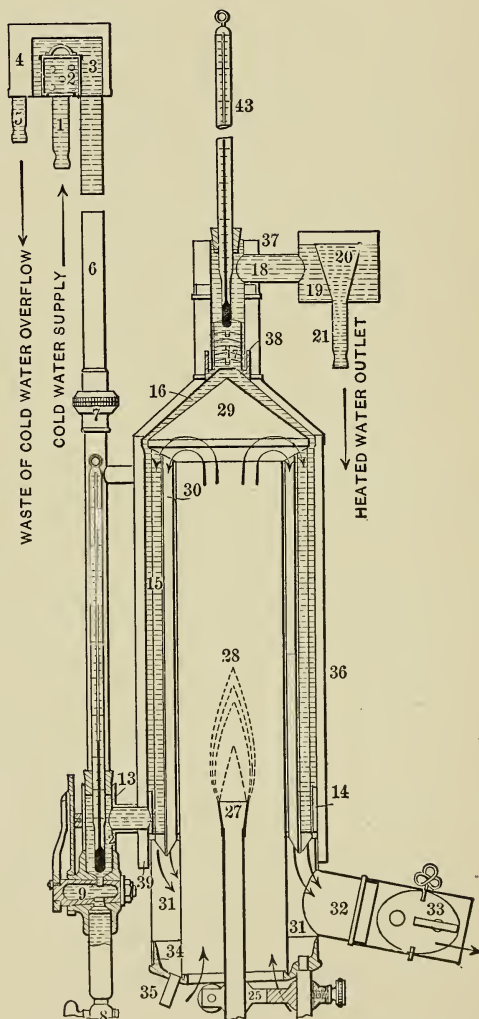
FIG. 16.—JUNKER GAS CALORIMETER (SECTION).

from an article by Kühne in the Journal of the Society of Chemical Industry, vol. 14, p. 631. As will be

seen from Fig. 16, this consists of a combustion-chamber, 28, surrounded by a water-jacket, 15 and 16, this being traversed by a great many tubes. To prevent loss by radiation this water-jacket is sur-
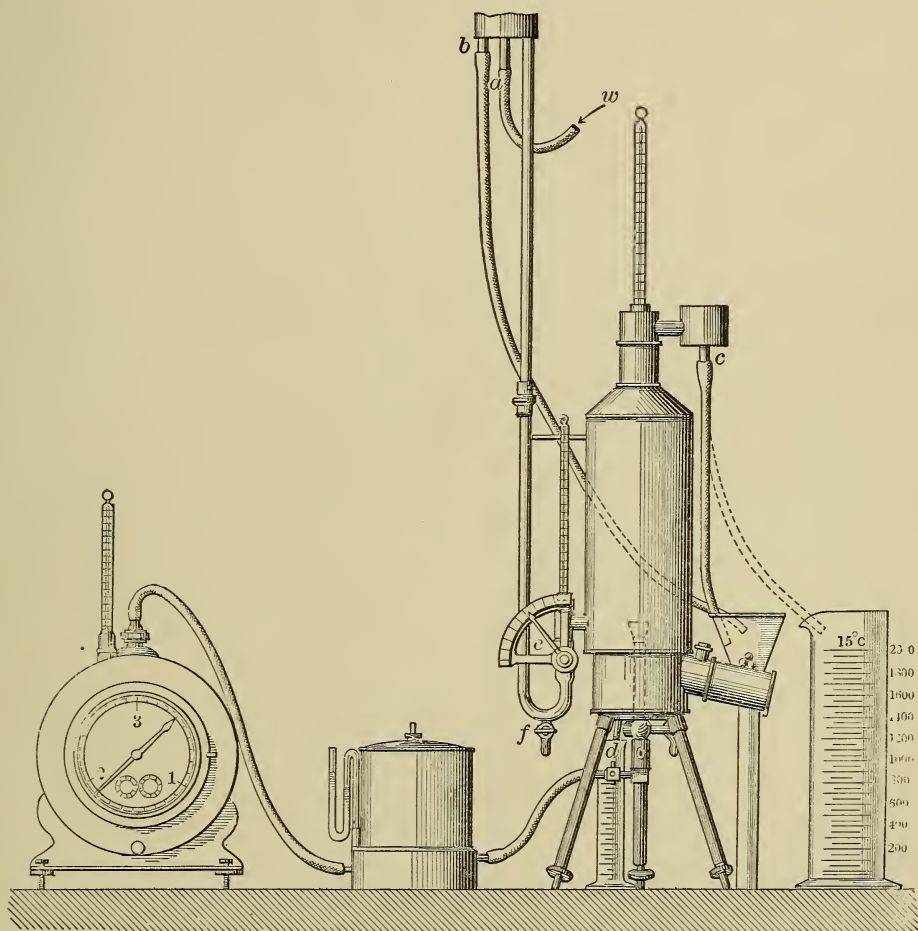
FIG. 17.—JUNKER GAS CALORIMETER.

rounded by a closed annular air-space, 13, in which the air cannot circulate. The whole apparatus is constructed of copper as thin as is compatible with strength. The water enters the jacket at 1, passes down through 3, 6, and 7, and leaves it at 21, while

the hot combustion-gases enter at 30 and pass down, leaving at 31. There is therefore not only a very large surface of thin copper between the gases and the water, but the two move in opposite directions, during which process all the heat generated by the flame is transferred to the water, and the waste gases leave the apparatus approximately at atmospheric temperature. The gas to be burned is first passed through a meter, Fig. 17, and then, to insure constant pressure, through a pressure-regulator. The source of heat in relation to the unit of heat is thus rendered stationary; and in order to make the absorbing quantity of heat also stationary, two overflows are provided at the calorimeter, making the head of water and overflow constant. The temperatures of the water entering and leaving the apparatus can be read by 12 and 43; as shown before, the quantites of heat and water passed through the apparatus are constant. As soon as the flame is lighted, 43 will rise to a certain point and will remain nearly constant.

Manipulation.—The calorimeter is placed as shown in Fig. 17, so that one operator can simultaneously observe the two thermometers of the entering and escaping water, the index of the gas-meter, and the measuring-glasses.

No draft of air must be permitted to strike the exhaust of the spent gas.

The water-supply tube *w* is connected with the nipple *a* in the centre of the upper container; the other nipple, *b*, is provided with a waste-tube to carry away the overflow, which latter must be kept running while the readings are taken.

The nipple *c* through which the heated water leaves the calorimeter is connected by a rubber tube with the large graduate. *d* empties the condensed water into the small graduate.

The thermometers being held in position by rubber stoppers and the water turned on by *e* until it discharges at *c*, no water must issue from *d* or from 39, Fig. 16, as this would indicate a leak in the calorimeter.

The cock *e* is now set to allow about two liters of water to pass in a minute and a half, and the gas issuing from the burner ignited. Sufficient time is allowed until the temperature of the inlet-water becomes constant and the outlet approximately so; the temperature of the inlet-water is noted, the reading of the gas-meter taken, and at this same time the outlet-tube changed from the funnel to the graduate. Ten successive readings of the outflowing water are taken while the graduate (2-liter) is being filled and the gas shut off.

EXAMPLE.—Temp. of incoming water, 17.2°
"   " outgoing   "   43.8°
Increase,   26.6°

Gas burned, 0.35 cu. ft.

$$\text{Heat} = \frac{\text{liters water} \times \text{increase of temp.}}{\text{cu. ft. gas}} = \frac{2 \times 26.6}{0.35}$$

$$= 152.3\text{C.}$$

From burning one cubic foot of gas 27.25 cc. of water were condensed. This gives off on an average 0.6 C. per cc.

$$27.25 \times 0.6 = 16.3C;$$
$$152.3 - 16.3 = 136 \text{ C per cubic foot};$$
$$136 \times 3.96828 = 540 \text{ B.T.U.}$$

The apparatus has been tested for three months in the German Physical Technical Institute with hydrogen, with but a deviation of 0.3 per cent from Thomson's value. This value may vary nearly that amount from the real value owing to the method which he employed.

b. By Calculation.

Oftentimes it may be impracticable to determine the heating value of gases directly; in such cases recourse must be had to the calculation of its calorific power from volumetric analysis of the gas.

To this end multiply the percentage of each constituent by its number as given in Table IV, and the sum of the products will represent the British Thermal Units evolved by the combustion of one cubic foot of the gas.* It is assumed that the temperature of the gas burned and the air for combustion is 60° F., and that of the escaping gases is 328° F., that corresponding to the temperature of steam at 100 pounds absolute pressure.

As has been already stated, column 3 in Table IV is based upon the assumption that the gas, and air for its combustion, enter at 60° F., and the products of combustion leave at 328° F.; in column 4 it is assumed that the entering temperature of both gas and air is 32° F., and the combustion-gases are cooled

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* H. L. Payne. Jour. Analytical and Applied Chem., 7, 230.

to 32° F. In case these conditions are varied, the amount of heat which the gas and air bring in must be determined; this is found in the usual way by multiplying the proportionate parts of 1 cubic foot, as shown by the analysis, by the specific heat of the gas, and this by the rise in temperature (difference between observed temperature and 32° F.). The quantity of air necessary for combustion is found by multiplying the percentage composition of the gas by the number of cubic feet necessary for the combustion of each constituent.

An example will serve to make this clear. The analysis of Boston gas is as follows:*

CO_2	"Illuminants."	O	CO	CH_4	H	N
2.9	15.0	0.0	25.3	25.9	27.9	3.0

Or in one cubic foot there are

.029 CO_2. .... .259 CH_4

.150 "illuminants"........ .279 H

.253 CO .... .030 N

Let us suppose its temperature is 62° F. The quantity of heat which one cubic foot of the gas brings in is then the sum of the heats of its constituents; this latter is its volume × volumetric specific heat × rise in temperature.

The "volumetric" specific heat is the quantity of heat necessary to raise one cubic foot of the gas from 32° to 33° F.; these are given in the Appendix, Table II.

---

* Jenkins, Annual Report Inspector of Gas Meters and Illuminating Gas, 1896, p. 11.

	Vol.		Vol. Sp. Ht.		Rise.	
"Illuminants" $= 0.15$	$\times$	0.04	$\times$	0.30	$.18$ B.T.U.
CO	$= 0.253$	$\times$	0.019	$\times$	0.30	$.14$
CH_4	$= 0.259$	$\times$	0.027	$\times$	0.30	$.21$
H	$= 0.279$	$\times$	0.019	$\times$	0.30	$.16$
CO_2N	insignificant.				

Total heat brought in by gas.... 0.69 B.T.U.

The quantity of air necessary to burn these several gases is, Table III :

"Illuminants" .... $0.15 \times 14.34 = 2.15$
CO............... $.253 \times 2.39 = .60$
CH_4............... $.259 \times 9.56 = 2.48$
H............... $.279 \times 2.39 = .67$

Theoretical quantity of air............ 5.90 cu. ft.
Add 20 per cent excess............... 1.20

Quantity of air used in burning 1 cubic
foot of Boston gas................... 7.10 cu. ft.

Assume its temperature to be $72°$ F.; then the heat it brings in is

$$7.1 \times .019 \times 0.40 = 5.4 \text{ B.T.U.}$$
Total gain is $\quad 5.4 + 0.7 = 6.1$ B.T.U.

Assume further that the gases, instead of passing out at a temperature of $328°$ F., leave at the same temperature as that of the chimney-gases, p. 29, $250°$ C. or $482°$ F.

The calculation of the heat carried away is similar to that there given.

0.15 cu. ft. of "illuminants" produces, Table III, 0.3 cu. ft. CO_2 and 0.3 cu. ft. steam;

0.253 cu. ft. of carbonic oxide produces .253 cu. ft. CO_2;

0.259 cu. ft. methane produces 0.259 cu. ft. CO_2 and .518 cu ft. steam;

0.279 cu. ft. hydrogen produces .279 cu. ft. steam.

From the combustion of the gas there results .812 cu. ft. CO_2, 1.097 cu. ft. steam, and 5.90 × 79.08 or 4.665 cu. ft. N.

The quantity of heat they carry off is as follows:

	Vol.	Vol. Sp. Ht.	Rise.	B.T.U.
CO_2............	.812 ×	.027 ×	450 =	9.9
N	4.66 ×	.019 ×	450 =	39.9
Excess of air..	1.2 ×	.019 ×	450 =	10.2
Steam.........	1.097 ×	.0502 ×	1229 =	67.7
Total heat lost.............. =				127.7

The loss due to the steam is found by multiplying the weight of steam found by the "Total Heat of Steam," as found from Steam Tables.* The tables, however, do not extend beyond 428° F.; it can be calculated by the formula

$$\text{Total heat} = \lambda = 1091.7 + 0.305(t - 32).$$

One cubic foot of hydrogen when burned yields .0502 lbs. of water.

The heat generated by the combustion of the gas is found by multiplying its volume by its calorific power, Table IV.

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* Peabody's Steam Tables.

"Illuminants" .... 0.15 × 2000.0 = 300.0 B.T.U.
CO.................... 0.253 × 341.2 = 86.3
CH$_4$................ 0.259 × 1065.4 = 276.0
H.................... 0.279 × 345.4 = 96.3
                                     ─────
Heat generated by the gas. .... 758.6 B.T.U.
Heat gained by rise in temperature
    of entering gas (62° F.) and air   6.1
    (72° F.)......................... ─────
                                       764.7
              Total heat lost............ 127.7
                                       ─────

                              637.0 B.T.U.

This figure, 637 B.T.U., represents the heating power of one cubic foot of the gas measured at 62° F., and is consequently too large; its heating value at 32° F. is represented by

$$\frac{492}{492 + 30} \times 637, \text{ or } 600.3 \text{ B.T.U.}$$

APPENDIX.

TABLE I.

TABLE SHOWING THE TENSION OF AQUEOUS VAPOR AND ALSO THE WEIGHT IN GRAMS CONTAINED IN A CUBIC METER OF AIR WHEN SATURATED.

From 5° to 30° C.

Temp.	Tension, mm.	Grams.	Temp.	Tension, mm.	Grams.	Temp.	Tension, mm.	Grams.
5	6.5	6.8	14	11.9	12.0	23	20.9	20.4
6	7.0	7.3	15	12.7	12.8	24	22.2	21.5
7	7.5	7.7	16	13.5	13.6	25	23.6	22.9
8	8.0	8.1	17	14.4	14.5	26	25.0	24.2
9	8.5	8.8	18	15.4	15.1	27	26.5	25.6
10	9.1	9.4	19	16.3	16.2	28	28.1	27.0
11	9.8	10.0	20	17.4	17.2	29	29.8	28.6
12	10.4	10.6	21	18.5	18.2	30	31.5	29.2
13	11.1	11.3	22	19.7	19.3			

TABLE II.

"VOLUMETRIC" SPECIFIC HEATS OF GASES.[*]

Air.....................	0.019	"Illuminants".........	0.040
Carbon dioxide..........	0.027	Methane................	0.027
Carbonic oxide..........	0.019	Nitrogen...............	0.019
Hydrogen..............	0.019	Oxygen................	0.019

The "volumetric" specific heat is the quantity of heat necessary to raise the temperature of one cubic foot of gas from 32° F. to 33° F.

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[*] H. L. Payne, *Jour. Anal. and Applied Chem.*, **7**, 233.

TABLE III.

THE VOLUME OF OXYGEN AND AIR NECESSARY TO BURN ONE CUBIC
FOOT OF CERTAIN GASES, TOGETHER WITH THE VOLUME OF
THE PRODUCTS OF COMBUSTION.

Name.	Formula.	Volume of Oxygen.	Volume* of Air.	Volume of Steam.	Volume of Carbon Dioxide.
Hydrogen	H_2	0.5	2.39	1	0
Carbonic oxide.	CO	0.5	2.39	0	1
Methane.......	CH_4	2.0	9.56	2	1
Ethane........	C_2H_6	3.5	16.73	3	2
Propane.......	C_3H_8	5.0	23.90	4	3
Butane........	C_4H_{10}	6.5	31.07	5	4
Pentane.... ...	C_5H_{12}	8.0	38.24	6	5
Hexane........	C_6H_{14}	9.5	45.41	7	6
Ethylene†......	C_2H_4	3.0	14.34	2	2
Propylene‡....	C_3H_6	4.5	21.51	3	3
Benzene§......	C_6H_6	7.5	35.85	3	6

* Air being 20.92 per cent by volume, 4.78 volumes contain 1 volume of oxygen.

† The chief constituent of "illuminants," new name "ethene."

‡ New name "propene."

§ Often called benzol, not to be confounded with ben*zine*.

TABLE IV.

CALORIFIC POWER OF VARIOUS GASES* IN BRITISH THERMAL UNITS
PER CUBIC FOOT.

Name.	Symbol.	60° initial. 328° final.	32° initial. 32° final.
Hydrogen..............	H	263.2	345.4
Carbonic oxide.........	CO	306.9	341.2
Methane...............	CH_4	853.0	1065.0
Illuminants†....	....	1700.0	2000.0
Ethane................	C_2H_6	....	1861.0
Propane...............	C_3H_8	....	2657.0
Butane........	C_4H_{10}	....	3441.0
Pentane...............	C_5H_{12}	....	4255.0
Hexane‡...............	C_6H_{14}	....	5017.0
Ethylene..............	C_2H_4	....	1674.0
Propylene.............	C_3H_6	....	2509.0
Benzene...............	C_6H_6	....	4012.0

* H. L. Payne, *loc. cit.*

† Where the ''illuminants'' are derived chiefly from the decomposition of mineral oil.

‡ The chief constituent of the ''gasolene'' used in the gas machines for *carburetting* air.

TABLE V.

SHOWING THE WEIGHT OF A LITER AND SPECIFIC GRAVITY REFERRED
TO AIR, OF CERTAIN GASES AT 0° C. AND 760 MM.

Name of Gas.	Weight, Grams.	Specific Gravity.
Carbonic oxide............... ...	1.251	0.967
Carbon dioxide.................	1.966	1.519
Hydrogen.....................	0.0896	0.069
Methane.....................	0.715	0.553
Nitrogen.....................	1.255	0.970
Oxygen.....................	1.430	1.105
Air........................	1.294	1.000

TABLE VI.

SOLUBILITY OF VARIOUS GASES IN WATER.

One volume of water at 20° C. absorbs the following volumes of gas reduced to 0° C. and 760 mm. pressure.

Name of Gas.	Symbol.	Volumes.
Carbonic oxide...................	CO	0.023
Carbon dioxide..................	CO_2	0.901
Hydrogen.......................	H_2	0.019
Methane........................	CH_4	0.035
Nitrogen.......................	N_2	0.014
Oxygen.........................	O_2	0.028
Air............................	....	0.017

TABLE VII.

MELTING-POINTS OF VARIOUS METALS AND SALTS, FOR USE WITH APPARATUS FIG. 11.

(From Carnelley Melting- and Boiling-point Tables.)

Alphabetically.		By Temperatures.	
Aluminium..........	660° C.*	Tin..................	233° C.
Antimony..........	432	Bismuth.............	268
†Barium chloride....	860	Cadmium............	320
Bismuth...........	268	Lead................	334
†Calcium fluoride....	902	Antimony............	432
Cadmium..........	320	Zinc................	433
†Cadmium chloride..	541	Cadmium chloride....	541
Copper............	1095	Aluminium..........	660*
Lead..............	334	Potassium chloride...	734
†Potassium chloride..	734	Sodium chloride......	772
†Sodium chloride....	772	Barium chloride......	860
Tin...............	233	Calcium fluoride......	902
Zinc..............	433	Copper..............	1095*

* Holman, Proc. Am. Academy, 31, 218.

† These salts must be dried at 105° C. to constant weight.

TABLE VIII.

GIVING THE NUMBER OF TIMES THE THEORETICAL QUANTITY OF
AIR SUPPLIED, WITH VARIOUS GAS ANALYSES.*

CO+O	$N = 79.$ $\frac{}{CO_2+O+CO=21}$	$N = 80.$ $\frac{}{CO_2+O+CO=20.}$	$N = 81.$ $\frac{}{CO_2+O+CO=19.}$	$N = 82.$ $\frac{}{CO_2+O+CO=18.}$
21	1.00	....	....	....
20	1.05	1.00	....	....
19	1.10	1.05	1.00	....
18	1.17	1.10	1.05	1.00
17	1.23	1.16	1.10	1.05
16	1.31	1.23	1.16	1.10
15	1.40	1.31	1.23	1.16
14	1.50	1.39	1.30	1.22
13	1.61	1.49	1.39	1.30
12	1.75	1.60	1.48	1.38
11	1.91	1.73	1.59	1.47
10	2.10	1.89	1.72	1.58
9	2.33	2.07	1.87	1.70
8	2.62	2.29	2.04	1.85
7	3.00	2.57	2.26	2.02
6	3.50	2.92	2.52	2.23
5	4.20	3.39	2.86	2.48
4	5.25	4.05	3.30	2.79
3	7.00	5.00	3.89	3.20
2	10.50	6.53	4.76	3.76
1	21.00	9.43	6.10	4.54

* Coxe, Proc. N. E. Cotton Manufacturers' Assoc., 1895.

TABLE IX.

COMPARISON OF METRIC AND ENGLISH SYSTEMS.

1 cubic inch	= 16.39 c.c.
1 cubic foot	= 28.315 liters.
1 Imperial gallon =	4.543 "

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1 lb. avoirdupois	= 453.593 grams.
1 calorie	= 3.969 B.T.U. (Röntgen).

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