THE EXAMINATION AND THERMAL VALUE OF

FUEL:

GASEOUS, LIQUID AND SOLID.

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PREFACE.

THE very kind reception accorded to the earlier work on *The Calorific Power of Gas* led to the writing of the present handbook, which may be regarded in some respects as a companion volume.

The examination of fuel of various kinds has for some years formed a considerable part of our official duties, and the present work is largely based on the experience so gained and on information gathered in connection therewith.

The subjects treated are not of a polemical nature, but we should make it clear that any opinions expressed are our own.

The basis and scope of this work are sufficiently indicated in the introductory Chapter.

Our best thanks are due, amongst others, to the following for permission to reproduce illustrations and the loan of blocks:—Prof. W. A. Bone, Dr. R. Lessing, The Cambridge Scientific Instrument Co., Messrs. A. Gallenkamp, The Proprietors of the *Colliery Guardian*, and Alex. Wright & Co.

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CHAPTER I.

INTRODUCTORY.

The Importance of Fuel as a Source of Power—Variations of Quality of Fuel—Availability of Methods of Examination—Scope of the Present Work—Limitations of Efficiency of Heat Engines—Vapourising Engines—Internal Combustion Engines.

The Importance of Fuel as a Source of Power.—With the exception of appliances worked by air or water power, which are to some extent being re-introduced, we are almost entirely dependent on fuel of some kind as a means of raising power. This circumstance, combined with the fact that expenditure on fuel is one of the greatest items of cost in modern industrial concerns, of necessity points to the need for economy in the use of fuel. From the broader cosmic point of view the conservation of a means of obtaining energy, which is present on the earth to a limited extent only, is of importance if we are to do our reasonable duty to posterity. Recent events have brought home to most of us the great dependence of all kinds of industry on fuel.

Great advances have been made by engineers in the economical application of fuel for various purposes. The total effect of small economies in the direction of ensuring more perfect combustion, of protecting appliances from losses by cooling, and of reducing the losses due to the escape of unduly hot products has been great.

Variations of Quality of Fuel.—Little attention has, in the past, been given to the fuel itself, owing partly to a vague idea that the supply is practically inexhaustible, and that variations in composition in the product of any one locality were small, and partly to the absence of any very definite means of estimating the relative commercial values of fuels. The modern use of fuels from a great variety of sources has rendered a more exact knowledge of their relative values desirable, and instruments and methods of technical application based on sound principles have been designed for or adapted to this purpose.

Availability of Methods of Examination of Fuel.—It will suffice in this chapter to state, without giving any technical details, that (1) methods of determining some of the physical properties, and the ultimate or proximate composition of solid, liquid, and gaseous fuel are available, and that the results obtained by the use of these methods can be given a more or less direct industrial significance; (2) the total amount of heat, measured in suitable units, given out by the combustion of practically any kind of fuel, can be determined with errors much less, at least in the case of solid fuel, than those incident to obtaining a sample representative of a large bulk. It is now, in fact, commercially possible to base contracts for fuel on a definite standard of heating value, with suitable allowances for excess or deficiency within reasonable limits, or on the ascertained cost per ton or other unit of delivery of a unit of heating value.

Scope of the Present Work.—In this work it is not proposed to deal with the business or engineering aspect of the examination of fuel, except in so far as it is necessary to the understanding of the subject, but rather to describe methods and appliances which have, in many cases within the authors' own experience, yielded results useful in the comparison and valuation of fuels, and to indicate the considerations on which opinions as to these points should be based.

As a matter of convenience, and to avoid needless repetition or cross references, the chemical and physical examination of fuel will be treated separately from fuel calorimetry, which is a subject by itself, and is more easily dealt with as such. The latter part of this work is based on a course of lectures on the "Calorimetry of Fuels," given by us at the Finsbury Technical College. Under the heading of the calorimetry of gaseous fuel only a few typical instruments have been described, as this subject has been more exhaustively treated by one of us in another work.

Some appliances have, for various reasons, been described, to which we can only give a very qualified approval. In each case the reasonable limitations within which good results can be obtained are indicated, as also is the reason for the inclusion of the appliance. Usually, however, descriptions are given only of methods and appliances which are based on definite scientific principles, or have been so carefully standardised as to give results which, until better can be obtained, are useful, even although their interpretation is purely empirical.

It is difficult to adapt a work of this kind to the varying requirements of those who may have occasion to use it, and to avoid irritating the chemist by minutely describing test tubes, on the one hand, or bewildering the engineer by assuming a profound knowledge of chemistry and physics, and great manipulative skill, on the other. We have endeavoured to give descriptions of the various processes sufficient to enable a worker with a fair experimental knowledge of "natural philosophy" to carry them out, and to acquire reasonable proficiency; but it should be obvious that scientific judgment and manipulative skill are very necessary for first-class work to be done. We consider that work of the kind described comes properly within the purview of the man who has been *trained* in the laboratory rather than, or as well as, on the works, and who knows the meaning of what he is doing.

It may be said, and with truth, that excellent practical work can be done by people who do not know the meaning of what they are doing. This is, we would point out, only the case when such workers are guided and supervised by, and their results subjected to the criticism of, those who know what they are doing. So many small points arise, which can only be cleared up by the aid of sound knowledge, experience, and clear judgment.

Limitations of the Efficiency of Heat Engines.—The fact that, in all cases where water or air power is not available, we are at present dependent on the combustion of fuel as an initial source of power is unfortunate, for heat engines are of necessity of very limited efficiency.

The maximum possible efficiency of such engines is determined by the ratio of the difference of temperature between the heated system and the condenser or exhaust to the absolute temperature of the heated system. Now, in practice, the height of the higher and the lowness of the lower temperature are limited, so that the ratio $\frac{T_1 - T_2}{T_1}$, where T_1 and T_2 respectively indicate the high and low (absolute) temperatures of working, never approaches closely to unity.

Vapourising Engines.—In a steam engine working with moist steam T_1 is obviously always below the critical temperature of water, 365° C., and T_2 is usually above 0° C., so that the efficiency of such an engine could not be higher than

$$\frac{365}{365 + 273}, \text{ or 57 per cent. ;}$$

in fact, such an efficiency is never approached in a steam engine, nor are such conditions obtainable, owing to various causes. It should be noted that in the above example it is assumed, among many other things, that the energy of the fuel is transferred completely to the engine. This is never the case, as all boilers (and steam pipes) are more or less inefficient. Even when unsaturated (superheated) steam is used the efficiency cannot be brought within reasonable approach to unity.

Internal Combustion Engines.—If one could burn the fuel direct in the engine, it would appear that a great economy might be effected. In the gas and oil engines this is done, and not only is the boiler loss done away with, but the initial temperature T_1 becomes very much higher, approaching that of the flame of the explosion. The good effect of this is much reduced by the circumstance that the temperature of the exhaust is also greatly raised. Nevertheless, the efficiency of the best internal combustion engines is usually much higher than that of the best steam engines. A few figures will give an idea of the relative efficiencies of steam and gas engines, and of the loss occurring in the boiler of the former engine.

The absolute thermal efficiency of steam engines may vary under the best conditions from about ·10 or under in the case of single-cylinder engines to ·17 to ·19 for triple-expansion engines, and up to ·23 for turbines. The actual working efficiency is frequently much less if the engine is not kept in good condition.

Internal-combustion engines will show an efficiency up to ·34 of the absolute thermal efficiency, and will maintain an efficiency approaching their best figures under actual working conditions.

Fuel as a source of motive power can, as stated above, be used either merely as a vapourising agency for obtaining an expanding substance in the steam engine, or the combustion may be made to take place wholly or in part in the engine itself. In the latter case it will always be found, except when natural gas or liquid fuel is used, that the fuel—coal gas, water gas, or producer gas—has itself been obtained by a heating process, and only represents a portion of the energy of the whole of the combustible material used. It is, nevertheless, often more economical to work in this way rather than to use the coal or other combustible direct for steam raising. It must also be borne in mind that, inefficient as all heat engines are as compared with, say, electric motors, where the loss of energy is extremely small, the latter engines are, where water power is not available—that is, in nearly all cases—dependent on fuel for the generation of electricity.

The enormous energy of the atoms of matter is not at present available for use by man, nor does the prospect of "harnessing" the atoms appear very hopeful. At present it is to the economical application and conservation of fuel that we must pay attention, always remembering that we are living on capital and not on income.

PART I.

CHEMICAL AND GENERAL PHYSICAL EXAMINATION OF FUEL.

CHAPTER II.

SAMPLING AND ANALYSIS OF GASEOUS FUEL.

I. Sampling.—Gas passing through a Shaft or Main—Collection of Small Samples—Sampling by means of a Simple Tube with Stopcocks—Huntly's Sampling Tube—Sodeau's Sampling Tube—Sampling Bottles—Solubility of Gases in Water.

II. Analysis.—Selective Absorption of Constituents—Explosion or Combustion—*Principles of Gas Measurement*—Typical Apparatus for Gas Analysis—(1) Sodeau's Apparatus, (2) Bone and Wheeler's, (3) Hempel's Burette—Absorption Pipettes—*General Points in Connection with Gas Analysis*—Mercury, Capillary Connections, Stopcocks—*Determination of Special Constituents of Gases*—Sulphur in all Forms—Carbon Monoxide—Methane—Loss of Heat in Flue Gases—*Recording Gas Analysis Apparatus for Flue Gases.*

I. SAMPLING.

Coal gas, water gas, and various kinds of "producer" gas are now very largely used as fuel either for furnace operations or for internal-combustion engines. It is, therefore, at times desirable to examine gaseous fuel with the object of determining the nature and relative proportions of its constituents, or for the purpose of ascertaining its calorific value.

Whatever may be the purpose of the examination, it is in every case necessary to take suitable precautions for obtaining a sample truly representing the bulk of the gas under consideration. This is not always a simple matter, and it will be well to indicate a few special cases, and the best methods of dealing with them.

Gas passing through a Shaft or Main is best sampled by means of as short an offset pipe as possible. If the service from the main is long, a considerable time of flow through the service may be necessary before the issuing gas can reasonably be assumed to have the same composition as that in the main. Differences of temperature in various parts of a long offset service may considerably reduce the probability of identity of composition. It is best in all such cases to arrange that gas shall be continually issuing (and burning) from the pipe, and the actual sample can then be taken from a second tap between the main and the point of issue (and burning). It is clear that a " dead end," or pipe full of stale gas, would yield samples which might differ very considerably from that flowing in the main. Flue gases can be collected in a similar manner, but it is necessary that the pipe inserted should be of a material—*e.g.*, porcelain or fire-clay—which will both stand the temperature at the place of intake and have no appreciable action on the constituents of the gas.

It is difficult to suggest any way of sampling gas in a large holder, as the composition is frequently by no means uniform, owing to variations during the making, and to the slowness of diffusion of gases which do not differ greatly in specific gravity. The only satisfactory plan appears to be to wait until the gas is issuing from the holder through a delivery main, and then either to take periodical samples, or to use some means, to be described later, of taking off a regular proportion of the flowing gas, and to examine the sample which has thus been automatically averaged. The same plan could obviously be adopted as the gas was being fed into the holder from the generating plant.

In the London Gas Act, 1905, the following clause prescribes the method of connecting the official gas testing places with the mains to be tested.

" 8. The company shall connect each testing place with such main or mains as may be prescribed by the Gas Referees by means of one service pipe only, which shall proceed direct from the main into the testing place, and there shall be no pipe branch or tap in any way connected with such service pipe outside the testing place except that the company may provide a tap on the service pipe at a point outside and as near as practicable to the testing place for use in case of emergency only . . ."

Collection of Small Samples.—It is not always convenient to examine gas *in situ*, as is implied in the above-mentioned clause, but frequently it is desirable to collect samples which are to be kept until they can be examined in a laboratory. Suitable vessels for the collection of such samples must, therefore, be provided, and these will vary in form and dimensions according to the nature of the work which is to be done on the samples.

Sampling by Means of a Simple Tube with Stopcocks.—Samples which are only required for analysis may in most cases be of very small dimensions. If an apparatus of the Frankland type, working with mercury as the confining liquid, at a reduced pressure, is to be used for the analysis, and for serious work apparatus of this kind is greatly to be preferred, samples of 50 cubic centimetres or less are sufficient. For the various kinds of apparatus in which water is used rather larger samples are required, since in most cases 100 c.c. are used for the actual analysis, and some difficulties of transfer may occur. We have found, for the smaller samples, a glass tube of the form shown in Fig. 1, of from 50 to 100 c.c. capacity and with *good* well-lubricated stopcocks, very satisfactory. It is not necessary that the tubular portions beyond the stopcocks should be of capillary bore, as they can easily be filled with mercury before the gas is transferred from them to the measuring apparatus, and thus all questions as to admixture of air with the gas be avoided. A sampling tube of this pattern is connected to a pipe from whence gas is issuing, by means of short lengths of rubber tubing, and the gas allowed to flow through the tube, both cocks being opened, until there is a reasonable certainty that the air originally in it has been expelled by the stream of gas. A rubber tube is usually attached to the outlet, so as to connect it with a burner, at which the escaping gas can be burnt. Half-an-hour will usually suffice to remove all air from a small sampling tube—that is, if a good stream of gas is allowed to pass through it. The glass stopcock further from the gas supply should be shut before the other, thereby preventing any backward diffusion of air. When both stopcocks are carefully closed they may be kept in position by rubber bands, so arranged as to press home the plugs, and the tube can, if desired, be packed in a fitted box. When a sample of gas cannot be analysed until a considerable time after it has been collected, it is better to use a tube as shown in Fig. 3, and described below, which

Fig. 1.—Gas sampling tube with stopcocks.

can be sealed by applying a small flame or blowpipe jet at A and B.

Gas from a suction plant only issues at a pressure below that of the atmosphere. It will, therefore, not flow out of a pipe leading to the air unless a sufficient exhaust is used. In such a case the sampling tube should either (1) be connected with the main by means of a pipe of negligible capacity—*e.g.*, a capillary tube—* and the sampling tube itself be filled with mercury or water, which, by its flowing out when the cocks are opened, will be displaced by the gas; or (2) an aspirator full of water must be connected to the outlet cock of the sampling tube, and a sufficiency of gas sucked through to remove all the air. Again a tube filled with water may be connected at its outlet with a vessel of water by means of a rubber tube, and connected to the main and washed out by alternately filling with gas, which may be contaminated with air from the connecting tubes, and blowing back the gas again into the main and sucking in fresh.

Sampling Tube.—G. N. Huntly † has described, as follows, a very good device (Fig. 2), based on Mariotte's bottle, for obtaining a continuous sample, over a period of some hours if desired, at a steady rate, of gas flowing in a pipe. It fulfils the following conditions:—

"1. Since mercury is used as the confining fluid, the sample tube must necessarily be small.

"2. The gas must be drawn into the sample tube at a uniform rate per hour.

"3. The gas in the dead space between the main tube and the sample tube must be eliminated.

"4. The gas in the sampling tube must not be allowed to diffuse back into the main tube, or to be drawn back into the main current by sudden changes of pressure.

"The usual pattern of tube, with single stopcock at each end, does not fulfil conditions 2, 3, or 4. The replacement of the single stopcocks by double ones, described by Haldane, eliminates the dead space difficulty, and much facilitates the transference of the gas in the laboratory. Stead's sampling tube also does not fulfil all the conditions."

"The tube figured satisfies conditions 2, 3, and 4. The gas

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* Capillary tubes of lead or "compo" piping can be obtained, and are very useful where a large service of piping is necessary. Failing an absolute capillary (1 mm. bore), "compo" pneumatic bell piping is convenient.

† *Journ. Soc. Chem. Ind.*, 1910, p. 312.

is drawn in at A. The dead space is cleared by sucking or allowing the gas to escape at B. The rate at which gas is drawn in is fixed by the tap and the distance C D, and the latter can be increased by joining on a glass tube with rubber to D. It is obvious that the gas cannot be sucked back or diffuse back. It has been found by trial that the rate at which the gas is drawn in is constant throughout within 1 per cent."

Sodeau's Sampling Tube.—Dr. W. H. Sodeau * "devised the tube described below after failing to find any description of a tube which, after having been sealed, could *readily* be placed in connection with the gas-measuring tube without risk of introducing air. It consists of a cylindrical bulb of, say, 200 c.c. capacity, joined at the upper end to a narrow tube drawn down to a capillary for sealing at A, and at the lower end to a tube of about 7 mm. bore, drawn down for sealing at the point B, about 4 or 5 cm. below the bottom of the bulb. When it is desired to collect a sample, the lower end is connected to a mercury

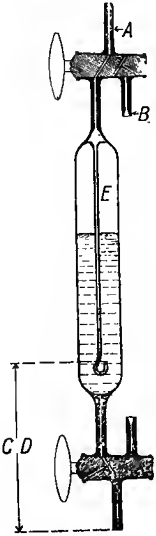

Fig. 2.—Huntly's gas sampling tube.

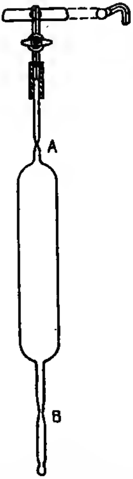

Fig. 3.—Sodeau's gas sampling tube with connections.

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* *Journ. Soc. Chem. Ind.*, 1903, p. 190.

reservoir by means of india-rubber tubing, and the upper to the bent capillary side tube of a T-piece (see Fig. 3), this arrangement being adopted in order that any condensed moisture may pass straight to the aspirator instead of entering the sample tube. After the sample has been collected, the tube is sealed at A and B in the usual manner. In order to transfer the sample, the lower tube is nicked with a glass knife near its junction with the bulb. The end B can then be easily broken off with the fingers beneath the surface of mercury in an ordinary porcelain trough. A crucible is then slipped under the open end, and the tube transferred to a vertical mercury trough, when a capillary syphon, filled with mercury, can readily be passed up through the open end of the tube, and the required portion of gas drawn into the measuring tube.

" A single cylindrical bulb can be used many times in succession by simply joining short pieces of tubing to either end and drawing them out for sealing. When it is desired to collect a sample during some definite period of time, the trouble of adjusting a stopcock so as to give the required rate of flow may be avoided by attaching a T-piece to the lower end of the sample tube and another to the india-rubber tube leading from the mercury reservoir. Two connections are then made (each capable of closure by means of a screw clip). The one utilised when filling the tube consists simply of a piece of pressure tube, whilst the other, used when collecting the sample, causes the mercury to pass through a drawn-out piece of capillary tube selected from a set of such pieces, which have been previously labelled, showing the time during which the mercury contained in the sample tube will run through under a given difference of level. The latter can, of course, be varied when some intermediate rate is desired " (Fig. 4).

This is also a thoroughly practical device.

Sampling Bottle.—Samples of gas sufficiently large for burning in calorimeters must be collected in special vessels. These need not be of an elaborate or costly nature. A Winchester quart bottle (A, Fig. 5) can be fitted with two tubes, one (*a*) passing through the cork and bent nearly to touch the side of the neck, and the other (*b*) only passing through the neck. Such a bottle can be filled with water, through the longer tube, from a reservoir or tap, and strong rubber tubes with pinch-cocks (*c*, *c*′) fitted to both tubes. When a sample of gas is to be collected, the bottle can be inverted and the gas allowed to bubble in through the longer tube, which is connected to the source of supply by means of a rubber or other tube, the water meanwhile being allowed to run out through the shorter tube, which can also be fitted with a tube to allow it to run away. When the bottle is full of gas it can be kept for a time with gas flowing through it, so as to reduce as much as possible the effects of the solubility in water of any of the constituents of the gas. By careful manipulation —*e.g.*, placing the bottle first on its side and then raising it to an inverted position—the amount of bubbling through the water may be greatly reduced. A better plan is to use a bottle with a tubulure at the bottom for an arrangement similar to the holder used with the calorimeter designed by one of us, and described later. In either case the use of a pointed metal rod (*d*), passed through the cork and pushed down so that contact with the surface of water is made, when from the full bottle a volume of water is taken equal to that intended to be burned of gas, will be found the most convenient and accurate way of gauging the delivery of a definite volume of gas when the bottle is put into use.

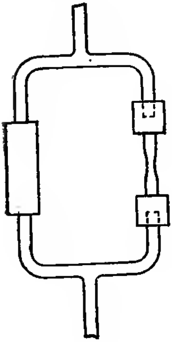
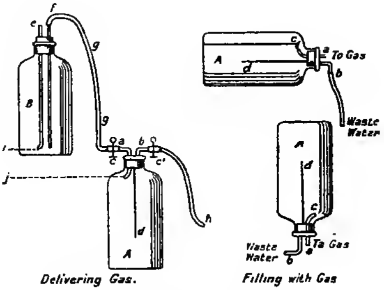


Fig. 4.



Delivering Gas. Filling with Gas

Fig. 5.—Bottle for collecting and delivering large samples of gas.

The corks of gas-sampling bottles should be carefully covered all over with melted paraffin wax, in which it is a good plan to soak them before finally fitting up the bottle, or with sealing wax, so that no cork is exposed. The upper end of the metal rod, which should, when adjusted, be cut off flush with the cork, should be well covered with sealing wax, so that it may be impossible to move it without chipping the wax.

When it is desired to burn gas from a bottle, such as has been described, it should be connected by rubber tubing with a bottle (*b*) or tubulated vessel containing water, and having a closely fitting cork fitted with tubes (*e*, *f*), as shown, the rubber connecting tube (*g*) should be filled with water, by suction if the syphon (*f*) is used, or by opening the tap or clip at the tubulure of the vessel, and then connected by a short piece of glass tube filled with water to the larger tube of the holder; the shorter tube is connected with the burner of the calorimeter. By opening the clips (*c*, *c′*) successively a flow of gas is obtained which can be regulated, by adjusting the tube (*e*)—this is best done in a preliminary experiment once and for all with air or gas—to the required rate for the calorimeter which is to be used. Air bubbles through *e*, and allows the water to flow from B to A at a constant rate determined by the height (*i*, *j*) and the resistance due to fluid friction in the system.

Solubility of Gases in Water.—In connection with both the sampling and the analysis of gas, it must be remembered that water dissolves most gases to an appreciable extent, and that the solubility varies with the temperature.

Table I. will show the extent of the variation of solubility of various gases ordinarily found in combustible mixtures or in the products of combustion.

It will be seen that a rise of temperature causes a decrease in the solubility, but that at 15° C., which is a fair average indoor temperature, the solubility is appreciable in the cases of all the gases named, and is considerable for some of the most valuable from a fuel point of view.

For sampling purposes it is usually possible to pass a sufficiently large volume of gas for the water adhering to the sides of the vessel to become saturated, but, except when analyses of gases of very similar composition are being made repeatedly in the same apparatus at temperatures not greatly differing, the use of water as a confining liquid is not altogether defensible, in spite of its cheapness and convenience as compared with mercury.

It must, of course, be remembered that the solubilities given in the above table are for a partial pressure of the gas of 760 mm., and would be correspondingly reduced when the gas was diluted with other gases—*e.g.*, from a gas measured at 760° mm., and containing 3 per cent. of ethylene—1 volume of water could only dissolve at 15°.

$$\cdot 139 \times \frac{3}{100} = \cdot 00417 \text{ volume,}$$

and that not immediately.

TABLE I.—VOLUMES OF GAS AT 0° C. AND 760 MM. BAR. DISSOLVED BY ONE VOLUME OF WATER AT t° C. WHEN THE PARTIAL PRESSURE OF THE GAS = 760 MM.

t = °C.	0	5	10	15	20	25	Authority.
t = °F.	32	41	50	59	68	77	
Oxygen, .	0·0489	0·04286	0·03802	0·03415	0·03102	0·02831	Winkler.
Hydrogen, .	0·02153	0·02061	0·01978	0·01903	0·01837	0·01780	Timofejew.
Nitrogen, .	0·02388	0·02153	0·01956	0·01786	0·01639	0·01504	Bohr and Bock.
Carbon monoxide,	0·03537	0·03149	0·02816	0·02543	0·02319	0·02142	Winkler.
Carbon dioxide, .	1·713	1·424	1·194	1·019	0·878	0·759	Bohr and Bock.
Methane, . .	0·05563	0·04805	0·04177	0·03690	0·03308	0·03006	Winkler.
Ethylene, . .	0·226	0·191	0·162	0·139	0·122	0·108	Winkler.
Propylene, . .	0·4465	0·3493	0·2796	0·2366	0·2205	. .	v. Than.
Acetylene, . .	1·73	1·49	1·31	1·15	1·03	0·93	Winkler.

Nevertheless, the solubility of gases is a sufficiently disturbing influence to render the use of mercury desirable in permanent laboratory apparatus which is to be used for accurate work.

The wetting of the sides of measuring vessels by water has some effect on the accuracy of measurement, and time should always be allowed for adhering water to drain before a reading is made. This trouble does not occur with mercury.

II. ANALYSIS.

It may be well, before describing any form of apparatus for the analysis of gases, to consider what sort of mixtures are presented for examination in the ordinary course of fuel practice. They are

Fuel gases which may contain	Combustible—H_2, CO, CH_4, C_2H_4. . . ., C_2H_2, C_6H_6 . . . . CS_2, H_2S. Incombustible—N_2, Ar, O_2, CO_2, H_2O.
Spent gases which may contain	Incombustible—N_2, Ar, O_2, CO_2, SO_2, SO_3, H_2O. Combustible—CO, CH_4.

Selective Absorption of Constituents.—Of these gases, the following can be removed from a mixture by the use of appropriate absorbents :—

CO_2, CS_2, H_2S, SO_2, SO_3, . .	Any alkali, usually KOH.
O_2, ...	Alkaline pyrogallol or yellow phosphorus.
C_2H_2, C_2H_4 . . . C_6H_6, . .	Bromine water or fuming sulphuric acid.
CO, ...	Acid or ammoniacal cuprous chloride.
H_2, ...	Palladium (seldom used).

Explosion or Combustion.—The following are usually determined by explosion or combustion with oxygen or air, and an examination of the residual gas :—

Gas.	Residue.
H_2, ...	Water, condensed.
CH_4, ...	CO_2, water.
N_2, Ar, ...	Unaltered, *if exploded under proper conditions.*

For example, a mixture containing $aH_2 + bCH_4 + cN_2$ will, on explosion with a proper excess of oxygen, yield

$$bCO_2 + cN_2 + (a + 2b)H_2O\ ;$$

and the loss of volume will be $aH_2 + \frac{a}{2}O_2 = \frac{3}{2}a$ for the combustion of free hydrogen.

The methane will require $2bO_2$, and the loss of volume will be $2b$.

The total loss of volume is, therefore, $\frac{3}{2}$ the volume of free hydrogen + 2 the volume of methane. Now, the volume of methane is equal to that of the CO_2 formed by its combustion, therefore a measurement of the loss of volume after explosion and of the CO_2 formed (*i.e.*, an absorption by KOH) will give the data for calculating the proportions of hydrogen, nitrogen, and CH_4.

$\frac{2}{3}$ (loss after explosion − $2CO_2$ produced) = hydrogen.
CO_2 produced = methane.
Difference from volume before introduction of oxygen = nitrogen.

If desired, the excess of oxygen may be exploded with excess of hydrogen, and $\frac{1}{3}$ the loss taken from the volume before introduction of hydrogen.

Principles of Gas Measurement—*Typical Apparatus for Gas Analysis.*—The above methods of absorption and explosion or combustion are generally used in actual work. It is not to be supposed that other methods cannot be used, but the experience of many workers is that those mentioned are useful, and in most cases trustworthy.

Now, since for a given mass of gas

$$\frac{\text{Pressure} \times \text{volume}}{\text{Absolute temperature}}$$

is a constant within reasonable variations of pressure and temperature, the relative amounts of the constituents of a mixture can be determined as proportional to

(1) Their volumes when pressure and temperature are constant;
(2) Their pressures when measured at constant volume and temperature;

(3) Their volumes when the ratio of pressure to (absolute) temperature is constant—that is, at constant elasticity—

and most gas analysis apparatus is so arranged as to comply with one or other of these sets of conditions. We will briefly describe typical apparatus of each class.

1. **Sodeau's Apparatus.**—Dr. Sodeau * originally based his apparatus on one described by Macfarlane and Caldwell, in which the gases to be measured are brought to atmospheric temperature, or to conditions very closely approaching this, before their volume is read. Dr. Sodeau's own description, slightly condensed, is as follows :—

The Measuring Apparatus (see Fig. 6).—The original device for raising and lowering the mercury reservoir, by means of a cord passing over pulleys and attached to a sliding block, is very convenient, as only one hand is employed in moving the reservoir, and it is very rarely necessary to use the clamping screw.

A cylindrical glass water jacket of 4 inches internal diameter, and 16 inches in height, is rigidly fixed to one of the uprights which guide the mercury reservoir, being supported at the bottom on a perforated block of compressed cork, *A*, and clamped at a point about 2 inches below the top, against a more or less crescent-shaped wooden block, *B*, by means of a strip of brass about 1 inch wide passing round the jacket, and tightened by means of a butterfly nut. A vertical strip of brass, about 2½ inches high and ¾ inch wide, serves to keep the capillary tube of the measuring vessel in position. The top of the jacket is closed by means of a split cork, which keeps the four upper ends of the measuring apparatus in position. In order that the movements of the mercury may be properly followed, it is important that the brass strip should not extend as high as the bottom of this cork. A glass tube *S* passes nearly to the bottom of the jacket, in order that the water may be readily syphoned off when desired ; for example, if it is advisable to alter its temperature.

The level-tube *L* is straight, having its lower end drawn out so as to pass through the india-rubber stopper closing the neck of the jacket, and its upper end fitted with an india-rubber stopper bearing a stopcock. The side branch leading to the measuring tube has a downward slope at the point at which it leaves the level-tube, but is bent upwards slightly beyond this in order to facilitate connection with the measuring tube *M*,

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* *Journ. Soc. Chem. Ind.*, vol. xxii., pp. 188-190, 1903.

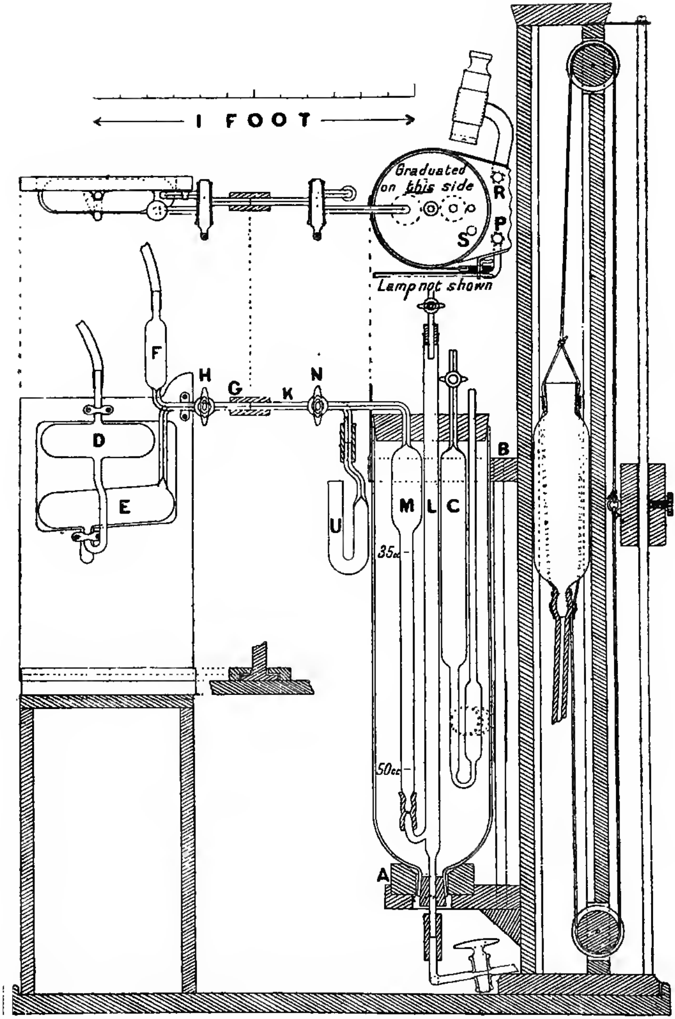

Fig. 6.—Sodeau's gas analysis apparatus.

by means of a short piece of india-rubber pressure tube. This arrangement prevents any air bubbles, accidentally entangled with the mercury, from reaching the measuring tube, and the india-rubber connection facilitates cleaning and simplifies the construction of the interchangeable measuring tubes. The measuring tube (verified at the Reichsanstalt) employed for the analysis of chimney gases, has at the top a cylindrical bulb, of about 26 mm. internal diameter, joined to a capillary which passes through the large cork, and below this bulb a straight stem graduated from 35 c.c. to 50 c.c. in $\frac{1}{10}$ c.c. divisions. The zero point of the graduation is situated at that side of the stopcock *N* which is furthest from *M*, as the gas is not expelled from the stopcock bore and inner part of the capillary before measuring. The capillary leading from the bulb terminates in a three-way oblique bore stopcock, with the plug placed horizontally in order to avoid the difficulty of driving gas down the markedly sloping bore of an oblique stopcock having its plug placed vertically. For other classes of work similar graduated tubes, either straight or with larger or smaller bulbs, may be substituted for the one figured. A small U-tube (*U*, Fig. 6) having one end joined to a bent capillary tube is partially filled with water, and connected to that branch of the stopcock *N*, which cannot be placed in connection with the bulb of *M*. The lower end of the level-tube is connected to a T-piece, one limb of which is provided with a stopcock of about 3 mm. bore,* and connected to the mercury reservoir, whilst the other is prolonged across the table to a point near the reading telescope (which stands on the same table), where it is connected to a short length of stout india-rubber tubing of $\frac{1}{4}$-inch bore, capable of being compressed by means of a screw clip, having a plate 1 inch in diameter instead of the usual bar. The apparatus stands at the edge of the gas analysis table, with the graduations, of course, turned towards the reading telescope; the cross pieces of the stopcocks are, therefore, placed on the ungraduated side—*i.e.*, the side from which the apparatus is manipulated. This reversal of the more usual arrangement leads to greater compactness by avoiding the use of a separate stand for the reading telescope, and permits the ready employment of the fine adjustment for levelling the mercury as described below.

The gas having been introduced into the measuring vessel, the stopcock at the top of the level-tube is opened and the mercury

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* The plug of this stopcock should taper but little, in order that it may not be forced out by the pressure of the mercury.

roughly levelled. The stopcock leading to the mercury reservoir is then closed in order to prevent oscillation, and the levelling completed without taking one's eye from the reading telescope by gently turning the milled head of the screw clip, so as to increase or diminish the capacity of the india-rubber tube referred to above.

In order that the surfaces of the mercury may be well illuminated a quarter-plate "focussing screen" has its upper half covered with copper foil, and a 2 c.p. electric lamp (not shown in Fig. 6) fixed opposite the centre and about 5 inches behind it. A split tube attached to this arrangement is slid up or down the rod *P* until the lower edge of the opaque part is just above the level of the mercury, the lamp being brought into use as soon as daylight becomes too weak.

A "Kew Principle" Correction Tube (*C*, Fig. 6).—A cylindrical bulb of capacity markedly exceeding 50 c.c. (see below) is sealed at the upper end to a small stopcock, and at the lower to a **U**-tube, of which the descending limb is graduated in $\frac{1}{20}$ c.c.,* whilst the ascending limb has a marked increase of diameter at a level corresponding to that occupied by the graduations of the other limb. After careful cleaning, this apparatus is fixed in the water jacket with both ends above the top of the large cork, and the cross-piece of the stopcock pointing towards the reading telescope, in order that it may be practically impossible for it to be turned by mistake during the analysis. This stopcock is opened and water introduced until the lower part of the meniscus roughly coincides with the line which is taken as the zero point. The instrument then requires no further attention until the water has been sensibly reduced by evaporation, except the momentary opening and closing of the stopcock immediately before an analysis is commenced, in order that the water may be brought approximately to the zero line, and large correction numbers thus avoided. Readings of this instrument may be taken by means of the ordinary reading telescope, but it is convenient to employ a reading lens similar to that sometimes attached to Stead's apparatus, consisting of a lens of, say, 5 inches focus mounted about 3 inches beyond a disc having a small hole like the cap of a small eye-piece, the whole being attached to a split tube sliding on the rod *R*. The corrections can thus be found as easily as a thermometer is read, and much trouble is saved by the use of this correction tube, although the usual form, in

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* A piece cut from a 10-c.c. graduated pipette answers very well.

which it is necessary to level the mercury in the two limbs before reading, seems of all but doubtful utility, as it is more trouble to adjust one of these than to successively read a thermometer and a good barometer constructed on the Kew principle.*

Let the capacity of the bulb, together with that of the portion of the tube which is above the zero point = X c.c., and let the atmospheric pressure be 760 mm., then if a change which would lead to a 1 per cent. increase of volume is to give 0·5 c.c. displacement of water, and this results in a disturbance of level amounting to N mm., it follows that—

$$1{\cdot}01\,X = (X + 0{\cdot}5)\left(1 + \frac{N}{760 \times 13{\cdot}5}\right) \therefore X = \frac{10{,}260 + N}{205{\cdot}2 - 2N}.$$

In a tube made by the author a movement of 0·5 c.c. disturbs the level to the extent of 16 mm.; hence X = 59·4 c.c. With this capacity above the zero mark one division ($\frac{1}{20}$ c.c.) corresponds to a correction of 0·1 per cent., and each of these divisions can be further subdivided into 10 by eye-estimation.

The above calculations are made on the assumption that the barometer is at 760 mm., but ordinary atmospheric variations do not cause a sensible error. Thus at 700 mm. the error introduced in correcting for 2° C., or 6 mm., amounts to only 0·01 per cent.

The correction tube can, of course, be used in nitrogen determinations, etc., if a reading is compared with the temperature and pressure at some time during the day.

Pipettes for Ordinary Absorbents.—The form shown in Fig. 6 differs from that of Macfarlane and Caldwell in two important points. Whilst the upper cylindrical bulb *D*, of about 60 c.c. capacity, retains its horizontal position, the lower cylindrical bulb *E*, of about 80 c.c. capacity, is slightly inclined, so that the end nearer the stopcock is about ¼ inch higher than the further end, in order that the unabsorbed gas may be returned to the measuring vessel without the troublesome necessity of tilting practically the whole of the apparatus, and then restoring it to its original position. Instead of a simple stopcock, the pipette is provided with the well-known device of a three-way oblique stopcock *H*, so arranged that the projecting capillary *G* can be

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* It seems difficult to understand the continued popularity of the Fortin barometer for ordinary rough chemical work, now that good Kew-system instruments can be procured with the National Physical Laboratory's certificate (Sodeau).

placed in connection with either the bulb *E*, containing about 20 c.c. of the absorbent confined over mercury, or with the bulb *F*, of about 15 c.c. capacity, containing mercury. The glass portion is mounted on a wooden support, the bottom of which slides freely into the groove of a wooden foot when in actual use. Whilst out of immediate use the bottom of each pipette is slid into a rack, which is inclined about 35° in order to relieve the pressure of the mercury, and thus prevent the absorbent from being forced through the stopcock. It is important that the end of the capillary *G* should be smooth, and at right angles to the axis of the tube, as any projecting pieces, either here or on the corresponding part of the measuring tube, will cause the introduction of an air bubble. The end of each capillary tube should, therefore, ordinarily be ground. It is also desirable that the external diameter of all capillary tubing used in the construction of this gas analysis apparatus should be about 6 mm., and that its bore should neither exceed 1·5 mm. nor be less than 1·0 mm. The tubes projecting upwards from *D* and *F* are each provided with a piece of india-rubber tube, about 6 inches long, in order that the pressure therein may be varied by drawing or blowing as required—a process much easier than that of moving a mercury reservoir.

Mode of Manipulation.—After introducing the gas into the measuring tube, the stopcock *N* is turned so as to connect the capillary *K* with the U-tube *U*. The pipette having been placed on a stool of appropriate height and connected to the measuring apparatus by means of a short piece of *really good* red india-rubber tubing of $\frac{1}{4}$ inch bore and $\frac{1}{2}$ inch external diameter, the ends of the two wetted capillary tubes are made to meet. A little water is then sucked through the capillary tubes into *F*, some of the mercury contained therein allowed to run back, and *H* closed. In this way the capillaries leading from the measuring tube to the pipette are washed out and filled with mercury. After measurment the gas is sent over into the pipette, followed by sufficient mercury to clear the capillary tube, and the pipette shaken from side to side with the stopcocks closed, in case the tube should by any chance slip off, until absorption is complete. The construction of the apparatus allows of efficient agitation, and in the nearly horizontal bulb a considerable surface of absorbent is exposed, so that there is more chance of the absorption being as accurate as the measurement than is the case in some well-known forms of apparatus. When absorption is judged to be complete a little more mercury is run over in order to clear any absorbent from that part of the capillary which is sealed to the bulb *E*, and the mercury in this capillary, instead of being returned to the measuring tube, is forced into *U*, the water in the latter affording complete safety as regards loss of gas; for, if the stopcock *N* should not be turned at the right moment, any gas passing over can be drawn back again. When the gas reaches *N* the stopcock is reversed, and the gas passes into the measuring tube, the rate being controlled by means of *H*. The constriction caused by this stopcock (nearly closed) brings the absorbent almost to a standstill when the gas has passed through, so there is no difficulty in stopping the absorbent when it has just filled the bore of the stopcock. The capillary is cleared of gas by means of clean mercury from *F*, this being stopped as soon as it reaches the stopcock *N*. In this way, nothing but gas is ever intentionally allowed to enter the measuring tube. These manipulations are really very easy, although the description may perhaps seem a trifle complicated.

When, as in the estimation of carbon monoxide, it is necessary to subject the gas to more than one treatment with an absorbent, the first pipette is brought into direct connection with the second, and the gas thus transferred from pipette to pipette until absorption is complete, when the gas is finally returned to the measuring tube. The manipulation in transference from pipette to pipette is practically the same as that between pipette and measuring tube.

A slight deviation is made when fuming sulphuric acid is employed, no mercury being then permitted to enter the bulb *E* or the capillary in immediate connection therewith. A U-tube containing pumice and strong sulphuric acid is attached to the bulb *D* in order to prevent access of moisture, and the mercury first used to clear the capillary should be driven into *F* before introducing the gas into the pipette.

The Explosion Pipette resembles that of Dittmar, except that the stopcock and capillary U-tube are replaced by a three-way stopcock and mercury bulb similar to those forming part of the absorption pipettes.

It will be seen that if it is not found to be feasible to maintain a constant temperature and pressure throughout the course of an analysis, a suitable small correction can be made by using the Kew principle correction tube. It is difficult to avoid small variations of temperature, and the device appears to be convenient. We have not used Sodeau's apparatus, but there seems to be no doubt that it is suitable for practically all classes of gas analysis.

2. **Bone and Wheeler's Apparatus.**—W. A. Bone and R. V. Wheeler have described * an apparatus based on Regnault's and Frankland's principle of measurement at constant volume, which we can personally testify is eminently suitable for the analysis of such complex mixtures as coal gas.

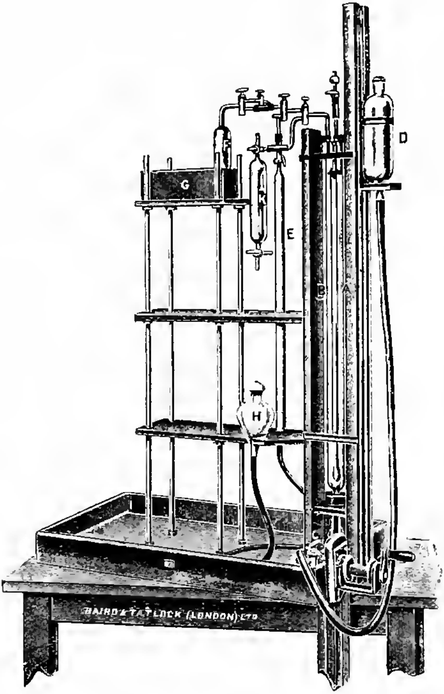

Fig. 7.—Bone and Wheeler's gas analysis apparatus.

They describe the apparatus and method of manipulation as follows :—

" It comprises essentially three parts—viz., (1) a water-jacketed combination of measuring and pressure tubes (*A* and *B*, Fig. 7)

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* *Journ. Soc. Chem. Ind.*, vol. xxvii., p. 10, 1908.

communicating through the glass tap *C* with the mercury reservoir *D*; (2) an absorption vessel *F* standing over mercury in a mahogany trough *G*; an explosion tube *E*, fitted with firing wires, and connected with a separate mercury reservoir *H*. All the connections between *A*, *E*, and *F* are of capillary bore throughout, with suitable glass taps wherever necessary. The diagram also shows how connection is made between the measuring tube *A* and the special 'sampling tube' *K* whenever the latter is employed for the introduction of the sample under examination. The sample may also be introduced into the apparatus from an ordinary test tube, under the wide open end of the absorption vessel *F*, which has been previously filled with mercury. Before commencing an analysis, the whole of the apparatus, including all the connections between *A*, *E*, and *F*, is completely filled with mercury, and, needless to say, the whole of the subsequent operations are conducted over mercury.

"The various parts of the apparatus are suitably mounted on a strong wooden stand, with four vertical rods supporting the shelf upon which the mercury trough *G* rests, the same rods also carrying another shelf for reagent bottles. Proper provision is made for the raising or lowering (to the ground level if required) of the mercury reservoir *D*, by means of a wooden carrier with suitable pulley and ratchet wheel. The whole apparatus stands in a wooden tray, 2 feet 4 inches by 1 foot 6 inches, with 1 inch raised sides.

"The salient features of the working of the apparatus are as follows:—

"(1) The principle of measurement employed is that first introduced into gas analysis by Regnault, and subsequently adopted by Sir Edward Frankland—viz., the measurement of the pressure of the gas (in mm. of mercury) at a constant volume. For this purpose the gas is brought to a certain 'constant volume' mark in the measuring tube *A* (by suitable manipulation of the mercury reservoir *D* and the tap *C*), and its pressure read off on the pressure tube *B*. There are a series of such 'constant volume' marks on *A*, each coinciding with a 100 mm. mark on the pressure tube *B* (*i.e.*, with 0, 100, 200, etc., mm.), so that the actual pressure of the gas is given by subtracting from the 'pressure reading' the numbers 0, 100, or 200, etc., according to the particular constant volume mark selected for the analysis. The tubes *A* and *B* are made in one piece, which is surrounded by a water jacket, and their inner surfaces are kept moist with very dilute sulphuric acid (1 in 20) as a precaution against the accidental fouling of the measuring tube with alkalies, and it is obvious that the wetting of *A* and *B* with the same liquid eliminates the influence of water vapour upon the gas measurements, the various pressures representing those of the dry gas under examination. The tap closing the upper end of the pressure tube is connected with it by means of stout rubber pressure tubing, a device which gives a perfectly tight joint with sufficient elasticity to prevent fracture in case the mercury in *B* is inadvertently allowed to run up the tube with unusual velocity. The tap in question also allows of the vacuum being easily made in *B* whenever necessary. The advantages of this mode of measurement over the more usual method of determining the volume under atmospheric pressure are twofold—viz., (1) it allows the use of smaller volumes of gas for an analysis; thus, from 5 to 10 c.c. of gas can be made to have a pressure of 100 mm., according to the particular volume mark selected, and this pressure can easily be read off to within ·2 mm. without employing a telescope; and (2) the measurements are, of course, independent of the barometric pressure, and at the same time are unaffected by tension of aqueous vapour.

"(2) The length of the pressure tube *B* (about 700 mm.) amply provides for the proper dilution of the 'explosive mixture' in an explosion analysis. . . .

"(3) The arrangements for the various 'absorptions' are of the simplest. All the absorptions are carried out over mercury in the one absorption vessel *F*, in each case with a comparatively small volume of the particular reagent, which is always used fresh, and is at once discarded after use.

"To facilitate the introduction of the various reagents, and the rinsing out of the absorption vessel with water or dilute sulphuric acid *in situ* between each successive reagent, the wide (open) end of the vessel is immersed under the mercury in the trough *G*, whilst the top terminates in a capillary three-way tap *R*. One of the parallel branches of this tap communicates, through a stout rubber joint, with the measuring vessel *A*, and the other with a water pump, a large bottle being inserted between the pump and the absorption vessel, to serve as a trap for either the mercury or the reagent which is being discarded after use. The insertion of a tap between the pump and the bottle obviates the necessity of the continuous exhaustion of the latter, a single exhaustion at the outset of the analysis being all that is required.

"From 2 to 5 c.c. of the particular reagent to be used is introduced into the absorption vessel (previously filled with mercury), by means of a suitable pipette, from below the surface of the mercury in the trough. Any minute bubble of air accidentally introduced with the reagent can be got rid of by cautiously opening the branch of the tap leading to the above exhausted bottle; the same device allows of the complete withdrawal of the reagent after use, and also of the rinsing out of the latter *in situ* with water or dilute sulphuric acid, before the next reagent is used."

This apparatus combines most of the advantages of the older forms designed by MacLeod and by Thomas, of which latter one of us can testify that, although apparently well designed, it was most difficult to work, and required frequent repair owing to its peculiar construction. It would perhaps be better with a longer pressure tube, but we cannot say that any serious inconvenience has been caused by the absence of this. It is suitable for actual measurements of the volumes of gases—*e.g.*, nitrogen, or a mixture of nitrogen and carbon dioxide obtained in organic analysis—if one or more of the divisions be calibrated, and is in our opinion suitable for all kinds of gas analysis. It has been used almost daily for the analysis of coal gas and similar mixtures.

We are inclined to give a strong preference to apparatus constructed for use on this principle of Regnault's and Frankland's, of measurement at constant volume, since very small quantities of gas can be manipulated, and it is much easier to obtain accurate millimetre scales than measuring tubes of uniform bore.

A particularly elegant apparatus for exact work has been designed by Mr. G. N. Huntly, and described in Travers' *Experimental Study of Gases* (1901 ed., p. 70).

Apparatus of the kind described above is, in our opinion, only suitable for use by those who are already expert manipulators. Many forms of apparatus have been designed, both for general gas analysis and for special purposes, for use by relatively unskilled workers. We find it difficult to approve of such appliances, although we realise that in many cases the temptation to use them is strong, and they are sometimes useful, if their limitations and those of their users are kept in mind.

Dr. Bone recommends the following reagents:—

(1) *Caustic Potash Solution* for the absorption of carbon dioxide and other acid gases. The contents of a 1-lb. bottle are dissolved in 500 c.c. of water. 1 c.c. of this solution will ordinarily suffice for each absorption, except when the absorption of carbon dioxide

is to be followed by that of oxygen by means of "alkaline pyrogallol" when 5 to 8 c.c. should be used.

(2) *Pyrogallol* for the absorption of oxygen. The contents of an ounce bottle are dissolved in 100 c.c. of water; the solution is stored, *without the addition of alkali*, in a narrow-mouthed stoppered bottle. When an absorption is to be carried out, about 2 c.c. of the solution are added to the 6 or 8 c.c. of caustic potash already in the absorption vessel. In this way the pyrogallol and the alkali are mixed in the absorption vessel, out of contact with air, and the absorbing power of the "alkaline pyrogallol" is unimpaired when the gas under investigation is put over it.

(3) *Bromine* for the absorption of unsaturated hydrocarbons (*e.g.*, ethylene). A solution of bromine in water containing 10 per cent. potassium bromide is employed, of such a strength as will not act on the mercury to any serious extent. The gas should always be subsequently treated with caustic potash solution before remeasurement.

(4) *Fuming Sulphuric Acid* containing about 10 per cent. of SO_3 may also be used for the absorption of unsaturated hydrocarbons.

(5) *Ammoniacal Cuprous Chloride* for the absorption of carbon monoxide, oxygen, acetylene, or ethylene.

From 50 to 75 grammes of cuprous chloride (*white* if fresh) are suspended in 250 c.c. of water in which 10 to 15 grammes of ammonium chloride have been previously dissolved. Ammonia gas is passed into the liquid (*which must be kept out of contact with air*) until no more of the solid is dissolved, and the solution distinctly smells of ammonia. About 5 grammes more cuprous chloride are added, and the liquid is then shaken, and set aside in a well (*india-rubber*) corked bottle. After standing for several hours, the solution should *not* smell of ammonia.

In an analysis, two successive portions of about 8 or 10 c.c. of the reagent are used, the gas being agitated with each lot of the liquid for *at least one minute.* Carbonic oxide is thus very rapidly, and for all practical purposes completely, removed, the whole operation not necessarily extending over more than five minutes; the gas is finally washed with dilute sulphuric acid (1 in 20) before remeasurement.

The rapidity and accuracy of the determination of carbonic oxide by this method depends entirely upon the care bestowed upon the preparation of the cuprous chloride solution, and its being used in a perfectly fresh and active condition. The analyst is recommended to test the absorbing power of the solution by means of a measured amount of pure carbonic oxide. An amount of the gas which gives a tension of 100 mm. at the constant volume mark O should be nearly all absorbed after one minute's agitation with 8 to 10 c.c. of a really active solution, and the absorption should be complete after a similar treatment with a second portion of the reagent.

Explosion Analyses.—These are carried out, in the usual manner, by explosion of the inflammable residue (after removal of oxides of carbon, oxygen, unsaturated hydrocarbons, etc.), with excess of oxygen (or air) free from carbon dioxide. The explosive mixture (" *Knallgas* ") should be diluted with at least twice its own volume of *excess* of oxygen, or air, and the explosion should be carried out under reduced pressure in the explosion vessel *E*. The oxygen is best prepared by gently heating recrystallised potassium permanganate in a small hard glass flask, and it should be washed through a strong solution of caustic potash. It may be conveniently stored in a small glass holder, with ground glass joints, over a mixture of equal volumes of glycerine and water; the holder is placed behind the shelves on the left-hand side of the apparatus, and suitable permanent connections of capillary glass tubing are made between the holder and the mercury trough *G* on the top shelf. The oxygen is added to the inflammable gas in the absorption vessel *F*, by means of a suitable delivery tube dipping under the surface of the mercury in the trough.

TABLE II.—ANALYSIS OF PRODUCER GAS.

	R.	T.	Vac.	Remarks.
	mm.		mm.	Gas taken = 166·75.
Original gas, . .	366·75	4·8	200	$CO_2 = 8·0 = 4·8\%$.
After KOH, . .	358·75	,,	,,	
,, pyrogallol, .	358·75	,,	,,	O_2 = *nil*.
,, ammon. Cu_2Cl_2,	312·9	,,	,,	$CO = 45·85 = 27·5\%$.
Oxygen added, .	420·0	4·8	200	C = 50·7.
After explosion, .	369·3	,,	,,	
,, KOH, . .	364·0	,,	,,	A = 5·3.
				$H_2 = 26·7 = 16·0\%$.
				$CH_4 = 5·3 = 3·2\%$.

Percentage Composition.—CO_2 = 4·8, CO = 27·5, H_2 = 16·0, CH_4 = 3·2, N_2 = 48·5.

Method of Recording Results.—Table II. shows how the analytical results are recorded.

Vac = "Vacuum" reading
R = Reading when the gas is brought to the constant volume mark selected.
(R − Vac. = Pressure of the gas.)
T = Temperature of water jacket.
C = Contraction on explosion.
A = Absorption by KOH after explosion.

3. **Hempel's Burette.**—W. Hempel has described a gas burette which is used very largely where moderate accuracy only is desired. It can be used with water or mercury, and is fairly easy to manipulate.

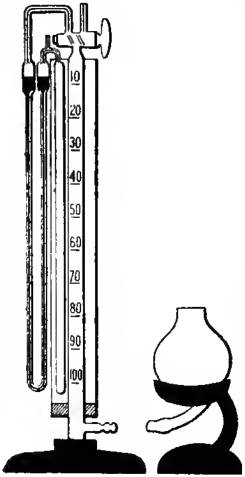

Fig. 8.—Hempel's gas burette.

A graduated burette (Fig. 8), to the top of which is sealed a two-way tap, is enclosed in a cylindrical water jacket. In this jacket also depends a long glass tube filled with air, and containing a few drops of water at the bottom. The upper part of this is connected with one limb of a long U tube containing mercury, which acts as a pressure gauge or equaliser, and the other limb of which is connected to one of the alternative passages of the stopcock of the burette.

The lower end of the burette is connected by rubber tubing to a mercury reservoir. Now gas can be drawn into the burette after (1) first raising the reservoir and opening the burette tap, so that the burette communicates with the air, and allowing all the air to escape; then (2) lowering the reservoir and turning the tap so as to draw over into the burette the air above the mercury in the pressure tube, and again turning the tap so as to expel the air thus drawn over. By connecting the burette, by means of the two-way tap, with a suitable rubber or metal tube, through which the gas to be analysed is flowing, and lowering the reservoir, a suitable amount of gas can be drawn into the burette. The mercury reservoir should now be manipulated until the surfaces of the mercury in it and in the burette are level, and the volume of gas taken into the burette measured. It is a good plan to have the mercury in the reservoir slightly higher than in the burette, and then, the gas supply tube having been disconnected, to open momentarily the tap to the air, so as to equalise the pressure. The burette is now connected to the pressure tube, and gas is driven over until the mercury in both limbs is level. The loss of volume in the burette—usually about 2 to 2·5 c.c.—is noted, and this volume is added to all future readings (a tube opening, when desired, to the air is sometimes attached to the top of the limb of the U, which is connected to the compensating tube, so that the pressure in the latter may be equal to that of the air when this is done. The compensator tube is now closed again). The gas is now all drawn into the burette, and the first absorption made by connecting a suitable pipette—*e.g.*, of the form shown in Fig. 9—containing the absorbing liquid with the burette by means of thick-walled narrow-bore rubber tubing, and driving over the gas into the lower bulb. After this and each absorption the gas is brought into the burette again, connection with the compensator opened, and the mercury levels in the U adjusted.

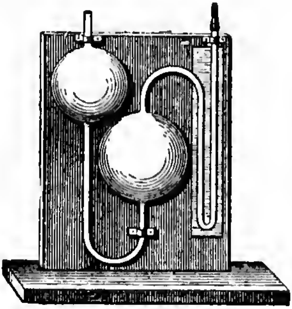

Fig. 9.—Hempel's gas pipette for absorption.

It is obvious that by this means of equalising the pressure of the gas with that exerted by a confined mass of air brought to constant volume, the relation

$$\frac{\text{Pressure}}{\text{Absolute temperature}},$$

that is, the elasticity of the various gases measured will be constant, and the volumes be strictly comparable. The gas is also compared with air saturated with water vapour.

The pipettes used for absorbents by Hempel are of the form shown in Fig. 9. The reagent is normally in the lower bulb, the tube at the top of which is of capillary bore, and only partly in the upper one. The capillary is connected to the burette by a suitable bent glass capillary and rubber connections, and the gas is forced into the lower bulb by raising the mercury reservoir and opening the stopcock. The pipette may be gently agitated to facilitate absorption. Although the capillary is fine, it is obvious that a slight loss or a slight fouling of the capillary of the burette tap must occur each time a pipette is changed. The fact that each reagent has its own pipette, necessitates the use of partly exhausted reagent after the first analysis, and has both advantages and disadvantages. In the first place the absorbents become saturated with the gases, which they are not supposed to absorb, and, therefore, after a time small errors due to this cause disappear, and in the second place they become less active as absorbents of the gases which they are supposed to absorb. A double pipette is used for oxygen, so that the alkaline pyrogallate may not rapidly become spent. On this point it should be noted that alkaline pyrogallate must be very alkaline. Clowes found * that, with a solution of 160 grammes of potassium hydroxide and 10 grammes of "pyro" in 200 c.c. of liquid, made by dissolving the potash in 130 c.c. of water, and then adding the 10 grammes of "pyro," no evolution of carbon monoxide from the solution took place. If the proportion of potash was small, serious error arose from this cause. The ammoniacal solution of cuprous chloride described by Bone is preferable to the acid solution frequently used.

Mr. A. F. Damon, senior gas examiner to the County of London, who has done a great deal of work with Hempel's burette, has kindly communicated the whole of the results of an analysis of mixed coal and water gas made by him, with some notes on his method of working. He tells us that he prefers to use water saturated with gas for the measurements previous to the explosion and water saturated with air afterwards. He has also abandoned the compensator, as he is able to work in a room of constant temperature.

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* *Chem. News*, lxxiv., 199.

TABLE III.—Analysis of Mixed Coal and Water Gas.

Volume of gas . . . . . = 100·0
Vol. after potash . . . . . = 97·8
,, bromine . . . . . = 93·0
,, alkaline pyro. . . . . = 92·2
,, cuprous chloride . = 75·0

Residue after CO, . . . = 75·0
Vol. taken for explosion . . . = 12·8
Vol. + air . . . . . . = 95·8
17·8 Contraction . . . . . . = 78·0
3·8 Vol. after potash . . . = 74·2

CO_2 . . . . = 2·2
O . . . . = ·8
Hydrocarbons . . . . . = 4·8
CO . . . . = 17·2
CH_4 . . . . = 22·2
H . . . . = 39·8
N . . . . . . = 13·0
Total . . . = 100·0

Illuminating power, ... 15·1 candles.
Calorific power (calorimeter), gross, . 136·2 Calories per cubic foot.
,, (,,), net, . 121·5 ,, ,,
,, (calculated), gross, . 133·5 ,, ,,
,, (,,), net, . 119·5 ,, ,,

Apparatus used—

Burette in water jacket and gas water.
Hempel's absorption bulb.
Explosion pipette (mercury).

100 c.c. gas taken (atmospheric pressure).
Gas passed into caustic potash bulb, drawn back after full absorption into burette, allowed to drain, and measured.

Result, 97·8 c.c. = 2·2 CO_2.

Gas passed into bromine bulb, then into caustic potash bulb, drawn back into burette, drained and measured.

Result, 93·0 c.c. = 4·8 hydrocarbon.

Gas passed into alkaline pyro bulb, drawn back, drained and measured.

Result, 92·2 c.c. = ·8 oxygen.

Gas passed into ammon. cup. chloride bulb, giving full time for absorption, drawn back into burette, allowed to drain, and measured.

Result, 75·0 c.c. = 17·2 CO.

The 75 c.c. gas was then passed over into another burette.

Burette was then washed out with HCl and water, and water used saturated with air.

12·8 c.c. gas was drawn into burette, and mixed with 83 c.c. air.

12·8 + 83 c.c. = 95·8 for explosion.

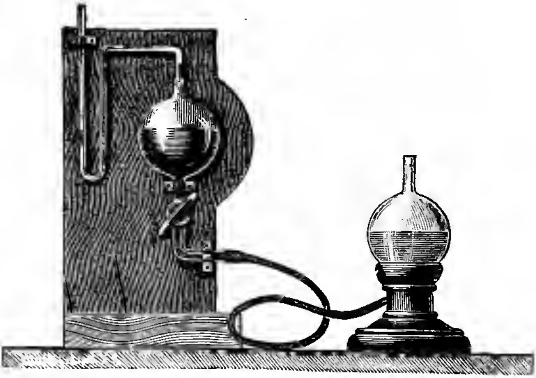

Fig. 10.—Hempel's explosion pipette.

The mixture of gas and air was then transferred to the explosion pipette (Fig. 10) and exploded.

Drawn back into burette and measured.

Result = 78·0 c.c. = 17·8 contraction.

Mixture then passed into caustic potash bulb, drawn back, allowed to drain, and measured.

Result, 74·2 c.c. = 3·8 CO_2.

Freshly prepared reagents were used, and all water was at the temperature of the room.

General Points in connection with Gas Analysis—*Mercury.*—This substance, it should be remembered, is about 13·5 times as heavy as water, and a movement of a column of 1 inch will effect as much difference of pressure as a movement of a water column through 13·5 inches. It is easy to drive gas from vessel to vessel too rapidly by moving mercury too quickly. One can also knock the top off a pressure tube or mercury pump by neglecting due caution in raising a mercury reservoir. It is also necessary that all taps and connections should be very sound in apparatus for use with mercury, owing to the great pressures which are set up.

Mercury is costly, and all mercury apparatus should be used on trays or on tables with a beading round them, so that any of the metal which is inadvertently spilt may not fall to the floor. It is also advisable to remove from the person all gold or silver watches, chains, rings, etc., or they may be badly damaged. It is wise to cover with cardboard or other suitable covers all vessels in which mercury is left exposed to the air. Dirty mercury may be cleaned by allowing it to fall in a fine stream through a long column of 5 per cent. nitric acid. A convenient apparatus for doing this is shown in Fig. 11. Mercury should be protected from contact with all metals except iron, which does not harm it. With most others it forms amalgams which interfere with its clean and well-defined surface when at rest, and cause it to adhere more or less to vessels containing it. Brass screws and collars should be avoided in apparatus for use with mercury, or should be well varnished with copal or other oil varnish.

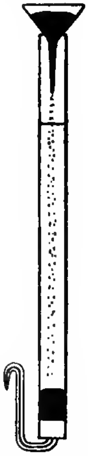

Fig. 11. Mercury cleaner.

Capillary connections should be of as small diameter as is compatible with free flow and convenience for keeping clean. A tube 1 mm. in diameter has a cross-section of ·785 mm., and a length of 1 decimetre or 4 inches will hold ·078 c.c. of gas. One 2 mm. in diameter has a capacity of ·314 c.c. per decimetre. Glass tubes, which it is desired to join temporarily, should be cut square and a piece about 2 inches or 5 or 6 cm. long of thick-walled rubber tubing of small bore slipped over their ends, which are then brought close together. The ends should be quite smooth and "square," so that no appreciable gas space may occur between them. Permanent or semi-permanent connections are best made by fusing the ends of the tubes together or by immersing the rubber-covered junction in mercury, water, or glycerine. This is seldom necessary in ordinary gas analysis.

Stopcocks.—Well-made stopcocks only should be used, and these require proper care. Nothing is much more annoying than to have a leaky stopcock, which under great differences of pressure passes gas round the barrel, or to find on using an apparatus which has been untouched for some time that the stopcocks are stuck, and must be heated and knocked and oiled and finally, most likely, broken.

The forms of stopcock most in use are shown in Fig. 12. *A* is the ordinary straight bore cock, which if well made and used is trustworthy, especially when the bore is small. It is somewhat liable to leakage around the barrel, as a groove is formed if the lubrication is not good. *B* is the same tap with a mercury jacket to prevent such leakage from having serious effects. It was formerly used, at any rate by us, to some extent for laboratory vessels in the Frankland apparatus for the analysis of gases from water residues. The plug is rather given to floating up. *C* is a stopcock designed and patented by Greiner and Friedreich, which cannot leak across the barrel. *D* is a similar stopcock with two alternative passages for the gas. *E* and *F* are other forms of three-way cocks. *E* is sometimes very useful. *F* has little to recommend it. It was formerly used largely on the Lunge nitrometer.

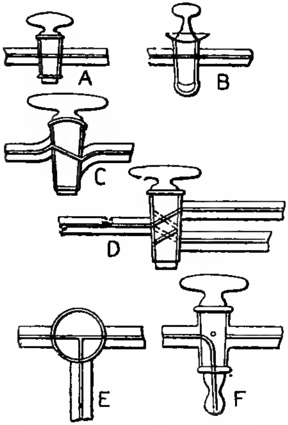

Fig. 12.—Glass stopcocks used in gas analyses.

Stopcocks must be properly lubricated. A good lubricant can be made by "dissolving" rubber in vaseline—a colloidal solution, not a true solution. We give two formulæ for making this lubricant. It is very much better than vaseline, "resin cerate," tallow, or any ordinary grease.

Sodeau employs a lubricant recommended by Prof. H. Jackson, of King's College, London. Six parts of black rubber (tubing), 5 parts of vaseline, and 1 part of solid paraffin should be heated together for some hours at a temperature sufficient to make the vaseline give off a fair amount of vapour. The process is complete when the whole of the rubber has dissolved. The heat employed must not be sufficient to burn the rubber.

Bone uses a mixture of 2 parts of soft rubber clippings, 1 part of vaseline, and $\frac{1}{10}$ to $\frac{1}{5}$ part of paraffin wax prepared in a similar manner. Travers uses a lubricant very similar to Bone's. The barrel of the stopcock to be lubricated should be taken out and both barrel and casing carefully wiped dry with a soft cloth. The barrel is then smeared evenly with grease, put in its place, and worked round until it fits smoothly. Care must be taken that the bore of the tap is not filled with grease. When stopcocks are used frequently they should be frequently lubricated, and when expected to be out of use for some time the plugs should be carefully taken out and put in a tray with cotton wool or other soft material. The seating of the tap should be covered or plugged with wool.

When a volumetric form of gas apparatus is used the accuracy of the divisions becomes a matter of importance, since, although it is easy to rule a millimetre scale on a tube (and better to have one behind it as in Huntly's apparatus), it is not as easy to divide a tube into equal volumes. The accuracy of division can be tested at such institutions as the National Physical Laboratory or the Reichsanstalt, or—*e.g.*, in the Hempel burette—water may be drawn into the apparatus over mercury and, maintaining it at constant temperature, delivered at each 5 or 10 c.c. into a weighed beaker. The relative volumes correspond to the weights observed; the absolute volumes, if required, can be obtained from tables of the specific gravity of water at various temperatures.

The calibration of various types of gas burette, and very many points of interest, will be found lucidly dealt with in Travers' *Experimental Study of Gases*. Useful information on such matters is also contained in Ostwald's *Physico-Chemical Measurements*, translated by Walker, or in the later German work by Ostwald and Luther. Hempel's *Methods of Gas Analysis* is also a book containing much useful information.

Determination of Special Constituents of Gases—*Sulphur*.—The determination of sulphur present in various forms in gases used for fuel (or for lighting) is a matter of importance. We give the Metropolitan Gas Referees' description of their method, which is used in London for official testings. We believe it to be trustworthy.

"The apparatus to be employed is represented by Fig. 13, and is of the following description:—The gas is burnt in a small Bunsen burner with a steatite top, which is mounted on a short cylindrical stand, perforated with holes for the admission of air, and having on its upper surface, which is also perforated, a deep circular channel to receive the wide end of a glass trumpet-tube. There are, both in the side and in the top of this stand, fourteen holes of 5 millimetres in diameter, or an equivalent air-way. On the top of the stand, between the narrow stem of the burner and the surrounding glass trumpet-tube, are to be placed pieces of commercial sesqui-carbonate of ammonia weighing in all about 2 ozs.

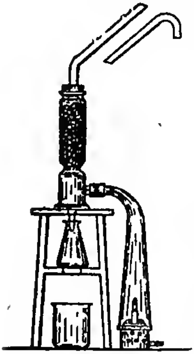

Fig. 13.
Gas Referees' sulphur apparatus.

"The products, both of the combustion of the gas and of the gradual volatilisation of the ammonia salt, go upwards through the trumpet-tube into a vertical glass cylinder with a tubulure near the bottom, and drawn in at a point above this to about half its diameter. From the contracted part to the top the cylinder is packed with balls of glass about 15 millimetres in diameter, to break up the current and promote condensation. From the top of this condenser there proceeds a long glass pipe or chimney tube slightly bent over at the upper end, serving to effect some further condensation, as well as to regulate the draught and afford an exit for the uncondensable gases. The chimney tube is suspended by a tape, tied round the middle of it and attached above to a bracket projecting from the wall, in such a manner that its lower end may be connected with or disconnected from the condenser with little change of position, or it may rest upon the bracket, being also attached to it by a girdle. In the bottom of the condenser is fixed a small glass tube, through which the liquid formed during the testing drops into a flask placed beneath.

"The following cautions are to be observed in selecting and setting up the apparatus:—

"See that the inlet pipe fits gas-tight into the burner, and that the holes in the circular stand are clear. If the burner gives a luminous flame, remove the top piece, and having hammered down gently the nozzle of soft metal, perforate it afresh, making as small a hole as will give passage to two-thirds of a cubic foot of gas per hour at a convenient pressure.

"See that the tubulure of the condenser has an internal diameter of not less than 18 millimetres, and that its outside is smooth and of the same size as the small end of the trumpet-tube; also that the internal diameter of the contracted part is not less than 30 millimetres.

"See that the short piece of india-rubber pipe fits tightly both to the trumpet-tube and to the tubulure of the condenser.

"The small tube at the bottom of the condenser should have its lower end contracted, so that when in use it may be closed by a drop of water.

"The end of the chimney-tube carries an india-rubber adapter or perforated plug, which, respectively, should fit over or into, and not simply rest upon, the top of the condenser.

"A central hole, about 50 millimetres in diameter, may with advantage be made in the shelf of the stand. If a beaker is kept on the table below, the liquid will still be preserved if by any accident the flask is not in its place.

"It is to be set up in a room or closet where no other gas is burning. The gas shall pass through a meter by reference to which the rate of flow can be adjusted, and which is provided with a self-acting movement for shutting off the gas when 10 cubic feet have passed.

"Pieces of sesqui-carbonate of ammonia, from the surface of which any efflorescence has been removed, are to be placed round the stem of the burner. The index of the meter is then to be turned forward to the point at which the catch falls, and will again support the lever-tap in the horizontal position. The lever is made to rest against the catch so as to turn on the gas. The index is turned back to a little short of zero, and the burner lighted. When the index is close to zero the trumpet-tube is placed in position on the stand and its narrow end connected with the tubulure of the condenser. At the same time the long chimney-tube is attached to the top of the condenser.

"As soon as the testing has been started, a first reading of the aerorthometer is to be made and recorded, and a second reading as near as may be to the time at which the gas is shut off. The rate of burning, which with practice can be judged very nearly by the height of the flame, is to be so adjusted that the meter hand shall make half a revolution in not less than four minutes.

"After each testing, the flask or beaker, which has received the liquid products of the combustion of the 10 cubic feet of gas, is to be emptied into a measuring cylinder, and then replaced to receive the washings of the condenser. Next the trumpet-tube is to be removed and well washed out with distilled water into the measuring cylinder. The condenser is then to be flushed twice or thrice by pouring quickly into the mouth of it 40 or 50 cubic centimetres of distilled water. These washings are brought into the measuring cylinder, whose contents are to be well mixed and divided into two equal parts.

"One-half of the liquid so obtained is to be set aside, in case it should be desirable to repeat the determination of the amount of sulphur which the liquid contains.

"The other half * of the liquid is to be brought into a flask, or beaker covered with a large watch glass, treated with hydrochloric acid sufficient in quantity to leave an excess of acid in the solution, and then raised to the boiling point. An excess of a solution of barium chloride is now to be added, and the boiling continued for five minutes. The vessel and its contents are to be allowed to stand till the barium sulphate has settled at the bottom of the vessel, after which the clear liquid is to be as far as possible poured off through a paper filter. The remaining liquid and barium sulphate are then to be brought on to the filter, and the latter is to be well washed with hot distilled water. (In order to ascertain whether every trace of barium chloride and ammonium chloride has been removed, a small quantity of the washings from the filter should be placed in a test-tube, and a drop of a solution of silver nitrate added; should the liquid, instead of remaining perfectly clear, become cloudy, the washing must be continued until on repeating the test no cloudiness is produced.) Dry the filter with its contents, and transfer it into a weighed platinum crucible. Heat the crucible over a lamp, increasing the temperature gradually, from the point at which the paper begins to char, up to bright redness.† When no black particles remain, allow the crucible to cool; place it when nearly

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* "If preferred a smaller proportion, say $\frac{1}{n}$th part of the liquid may be taken for the determination, in which case the number of grains of barium sulphate obtained must be multiplied by $\frac{11}{8}n$ instead of being multiplied by 11 and divided by 4.

† "An equally good and more expeditious method is to drop the filter with its contents, drained but not dried, into the red-hot crucible."

cold in a desiccator over strong sulphuric acid, and again weigh it. The difference between the first and second weighings of the crucible will give the number of grains of barium sulphate. Multiply this number by 11 and divide by 4; the result is the number of grains of sulphur in 100 cubic feet of the gas.*

"This number is to be corrected for the variations of temperature and atmospheric pressure in the manner indicated under the head of Illuminating Power, with this difference, that the mean of the first and second aerorthometer readings shall be taken as the reading.

"The correction by means of the aerorthometer reading may be made most simply and with sufficient accuracy in the following manner:—

"When the aerorthometer reading is between ·955-·965, ·965-·975, ·975-·985, ·985-·995, diminish the number of grains of sulphur by 4, 3, 2, and 1 per cent.

"When the aerothometer reading is between ·995-1·005, no correction need be made.

"When the aerorthometer reading is between 1·005-1·015, 1·015-1·025, 1·025-1·035 increase the number of grains of sulphur by 1, 2, and 3 per cent.

"Example:—

Grains of barium sulphate from 5 cubic feet of gas, ...	10·4	Aerorthometer reading 1·018.
Multiply by 11 and divide by 4, . .	11	
	4)114·4	
Grains of sulphur in 100 cubic feet of gas (uncorrected), ...	28·60	
Add 28·6 × $\frac{2}{100}$ = . .	·57	
Grains of sulphur in 100 cubic feet of gas (corrected), ...	29·17	Result: 29·2 grains.

"The aerorthometer reading is the reciprocal of the tabular number. The gas examiner shall, not less often than once a month, compare the aerorthometer reading with the reciprocal of the tabular number deduced from observations of the baro-

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* "233 grains of barium sulphate are formed from 32 grains of sulphur; *w* grains of barium sulphate have been obtained from 5 cubic feet of gas. Hence in 100 cubic feet of gas there are $\frac{32}{233} \times \frac{100}{5} = \frac{11}{4} w$ grns. of sulphur."

meter and thermometer, and if there is a difference of more than ½ per cent. the aerorthometer is to be readjusted."

The method which is described with such detail by the referees depends on the fact that the sulphur present in gas, principally as carbon disulphide and similar compounds, is burnt, not merely to SO_2, but to SO_3, provided that the products of combustion are not cooled too rapidly (*cf.* Chap. IX., correction for sulphuric acid formed in bomb). The SO_3 is caught at the top of the trumpet-tube, and in the condenser as ammonium sulphate, sufficient ammonia for this purpose being evolved from the ammonium carbonate placed around the flame. A great deal of the ammonium sulphate collected in the condenser is washed into the beaker by the water from the burning of the gas.

The aerorthometer is an instrument in which a confined volume of air is used to give a correction for the combined effects of variations of temperature and pressure from the standard conditions (under the Gas Acts) of 60° F. and 30 inches bar. It is clearly not the only instrument which could be used for this purpose.

It is generally realised that sulphur is an undesirable constituent in gaseous fuel, although opinions as to the extent to which it should be removed vary. It is a matter of expediency rather than of principle, for no one wishes to leave an excessive amount of sulphur in gas, but gas managers have felt that the use of lime to remove those compounds which are not absorbed by moist oxide of iron is so costly, inconvenient, and offensive that it should be abandoned, and the feeling has received sympathetic treatment from Parliament. On the other hand, oxide of iron removes a great deal of the impurity, which can, in this case, be converted ultimately into sulphuric acid and used to absorb the ammonia from the gas liquor, and in some cases great and successful efforts to effect further purification without using lime have been made since relief from the " sulphur clauses " was granted to the Metropolitan Companies.

The limits allowed formerly in the Metropolis were 22 grains of sulphur in 100 cubic feet of gas in the winter and 17 grains in the summer. The late Sir George Livesy considered 35 grains a reasonable average amount. The amounts actually found vary from much above this to much below. On the whole, at any rate in the Metropolis, the tendency is for a decrease. It is to be hoped that efforts in this direction may be rewarded by the conversion of all the sulphur so removed into a saleable form, not into the very troublesome " gas lime " of the past.

We would call attention to the fact that town gas is not the only fuel which contains sulphur, and that producer and other gases are equally likely to contain more sulphur than they ought; and, further, that all the sulphur in commercial fuel gases is obtained ultimately from the solid or liquid fuel used in their manufacture. The injurious effects of sulphuric acid on metal work are well known, and the presence of an excessive amount of sulphur in fuel, for internal-combustion engines more especially, is to be condemned.

Carbon Monoxide.—The determination of carbon monoxide, especially when present in very small quantities, can conveniently be made by means of the reaction occurring between it and iodine pentoxide. The gas is oxidised to CO_2 and iodine is liberated. This action occurs at temperatures of 60° C. and above. The liberated iodine is usually estimated by titration, but it is also possible to measure the carbon dioxide produced. Dr. L. A. Levy has described * an apparatus in which this is done. The gas, freed from unsaturated hydrocarbons (which have a retarding effect on the reaction) by passing it through a solution of bromine in potassium bromide, and from bromine vapour and carbon dioxide by potash, is passed over a drying tube of phosphorus pentoxide, and then through a U tube containing the iodine pentoxide. This is sealed to another U tube packed with copper turnings to absorb the iodine liberated, and both tubes are put in an air bath which is heated to 170° C. It is then passed through a tube similar in form to a Winkler absorption worm, but with rather steeper coils. This contains a definite amount of baryta solution of known strength, which is tinted with phenolphthalein. Gas is drawn through the apparatus by an aspirator, which is graduated so that the volume of water which has flown out of the apparatus at the moment of decolouration of the baryta solution shall indicate the percentage of carbon monoxide in the gas. The sensitiveness of the method obviously becomes less as the percentage of carbon monoxide increases. The results quoted by Dr. Levy, however, compare well with those obtained by absorption with cuprous chloride.

The reaction with iodine pentoxide is, in our opinion, more particularly suitable for the determination of small quantities of carbon monoxide in flue gases or for other cases where the gas may be present in small quantities rather than for coal or water gas as it is used by Dr. Levy, and for such purposes

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* *Journ. Soc. Chem. Ind.*, vol. xxx., p. 1437, 1911.

it is better to determine the iodine rather than the carbon dioxide.

Methane.—The determination of methane when present in small quantity is at times very important, especially, of course, in mine air. Flue gases may sometimes contain a very small percentage of this gas, the presence of which is evidence of serious errors in the construction or management of the furnaces. The quantities found in such cases are not usually large enough for the explosion process to be applicable unless electrolytic gas ($2H_2 + O_2$) is added to induce an explosion.

Combustion on the surface of a platinum wire heated by an electric current is usually resorted to in such cases. Haldane has designed an apparatus for the examination of mine air, in which a short platinum spiral in a bulb-shaped glass vessel is used for inducing the combustion. It is fully described in his *Methods of Air Analysis*, pp. 9, *et seq.*

Hempel and Levy * have independently designed somewhat similar apparatus. Levy uses a very convenient quartz glass capillary in which is stretched, by means of molybdenum spring terminals, a platinum wire, and passes the air, which, of course, contains a sufficient amount of oxygen for the combustion, through the tube into another vessel from the measuring burette. This tube can easily be used with any ordinary gas analysis apparatus if a little ingenuity is exercised, or it can be used in the special form of apparatus described by Levy (*loc. cit.*). The alteration of volume is a loss—is twice the volume of the methane burnt—and the volume of CO_2 formed is equal to that of the methane

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

Loss of Heat in Flue Gases.—The composition of flue gases from the furnaces of a steam boiler or of the exhaust gases from an internal-combustion engine, as already indicated, furnishes a good idea of the satisfactoriness, or otherwise, of the combustion arrangements.

To take the simplest case of complete combustion, the gases will contain, in addition to water vapour, which is in part derived from the combustion of the hydrogen of the fuel, and traces of oxides of sulphur, only nitrogen, oxygen, and carbon dioxide. Now, the percentage of nitrogen affords an index of the ratio of the amount of air passing through the furnace or cylinder to that

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* *Journ. Soc. Chem. Ind.*, vol. xxxi., p. 1153, 1912.

of the exhaust gases, since the chemical changes affecting the nitrogen are negligible, and its proportion in air is practically unvarying.

Air contains (by volume)—

Oxygen,	(20·91 to) 21·0	
Nitrogen,	78·05	79
Argon,	0·95	
Carbon dioxide,	(variable, probably always an impurity due to animal life, ·03 or less).	

For our purposes the figures 21·0 for oxygen and 79 for nitrogen and argon are all that need be considered. It follows from these that 1 part of nitrogen in the spent gases corresponds to 1·266 parts of dry air passing through the furnace or cylinder, and that this air would contain ·266 part of oxygen. Also, 1 part of carbon dioxide in the flue gases corresponds to an equal volume of oxygen in the air. We are, therefore, in a position to calculate the total air used, and the proportions of its oxygen used in burning the carbon and hydrogen by determining the nitrogen, oxygen, and carbon dioxide.

A determination of carbon monoxide will show whether and to what extent combustion is incomplete. This at times may need to be supplemented by a determination of methane, especially when burning oil fuel.

Since equal volumes of CO_2, CO, and CH_4 contain the same amount of carbon, the amount of CO_2 divided by the sum of the CO_2, CO, and CH_4 will show the proportion of the carbon of the fuel which is completely burnt. The presence of methane, as a reference to Table XXXI. will show, indicates a much more serious loss of heat than an equal volume of CO would.

Now, if the composition of the fuel is known, the amount of air required for its combustion, or at any rate the amount of carbon dioxide which should be produced by its combustion, can be calculated, as can also the amount of water (1) volatilised moisture of the fuel, (2) produced by combustion of the hydrogen. In the case of coal, an allowance may have to be made for the unburnt carbon in the furnace ashes.

One gramme of carbon burnt will produce 1·86 litres of CO_2, CO, or CH_4, or 1 lb. will produce 847 litres (about 30 cubic feet), so that the weight of fuel burnt, the relation which the carbon actually burnt bears to this, and the analysis of the flue gases will give the ratio which the weight of fuel bears to the volume of flue gases. The percentage of nitrogen in the flue gases will, of course, show the amount of dry air entering the furnace, since ·79 volume of nitrogen (and argon) corresponds to 1·00 volume of dry air.

The analysis of the flue gases, as usually performed, takes no account of the water vapour accompanying them. Its amount is clearly indicated by the sum of the water obtained from the fuel when burnt and that associated with the incoming air. As the latter is seldom more than 2 per cent. of the volume of the air, the magnitude of this correction is so much less than the probable error of the whole correction that it may be neglected, as in some cases can that caused by the moisture of the fuel (not the water formed by combustion). The thermal capacity of the gases can be calculated from their specific heats, which are given in Table IV.

TABLE IV.—SPECIFIC HEAT OF GASES.

Gas.	Range of Temperature.	Specific Heat.	Observer.
Air, . .	20-440° C.	0·2366	Holborn and Henning.
Nitrogen, . .	300° C.	0·2407	,, ,,
Oxygen, . .	20-440° C.	0·2419	,, and Austen.
Carbon monoxide,	23- 99° C.	0·242	Wiedemann.
Carbon dioxide, .	300° C.	0·2016	Holborn and Henning.
Water vapour, .	300° C.	0·4641	,, ,,
Methane, .	. .	0·591	Lusanna.

For most purposes it may be taken that the specific heats of the first four gases are all ·24, that of CO_2 is ·20, and of water vapour ·46; or the total heat of water vapour at 300° C. may be taken as 712 calories per gramme. It is not well known above 180° or 190° C.

If it be remembered that 1 lb. of carbon in burning gives rise to 847 (say 850) litres of $CO_2 + CO + CH_4$ at 0° C. and 760 mm., the following values may be used :—

Gas.	Thermal capacity of 1 litre at 0° C. and 760.
CO and N, ...	·30 calorie.
CO_2, ...	·395 ,,
O_2, ...	·345 ,,
CH_4, ...	·42 ,,

We can calculate thus, so many pounds of fuel are burnt, which contain, say, a lbs. of carbon. The volume of carbon gases produced is, therefore, 847 a litres per pound. The thermal capacity of this amount is $847\, a \times {\cdot}395$ calorie. In like manner the thermal capacity of the volumes of the other constituents of the flue gases can be calculated. The last point where the heat of the gases can be utilised is the economiser, where they are allowed to heat the feed water for the boiler, and it is as they leave here that their temperature should be taken. They have been heated from the temperature of the stokehole, and their loss is equal to their thermal capacity × the rise of temperature + the latent heat of the total water volatilised in burning the coal. It is good enough to take this as $L_t = 539 - {\cdot}64\ (t - 100)$ calories, where $t =$ the temperature of evaporation. As this temperature is not known, it is convenient to consider it as that of the stokehole, which is below 100°, so that the formula becomes

$$L_t = 539 + {\cdot}64\ (100 - t).$$

It must be remembered that a large amount of this loss is inevitable. In the first place, if the flue gases were cooled to the temperature of the boiler, a forced draught, either positive or negative, would be needed; hence some of the outgoing heat is doing the work of bringing the air in contact with the fuel—a most necessary operation for combustion. The loss of total heat of the outgoing water vapour, at least up to the minimum temperature necessary for the maintenance of the draught, is inevitable. The only losses which are avoidable are those due to excess of air and to imperfect combustion. These can be kept down by proper furnace construction, careful regulation of the draught, and analysis of the flue gases.

The foregoing calculation, it should be remembered, depends for its accuracy on the sampling and analysis of the gas, the correctness of the values taken for the specific heats of the constituents of the gas at the temperatures under consideration, or rather the correctness of the estimate of total heat based on these values, as also on the measurement of temperature of the flue gases, and it is probable that only the first two figures in any such calculation are really significant. The upper rule of a 10-inch slide rule would probably give a result more than good enough arithmetically, considering the inexact character of the data. Also, we have given the thermal values in calories; it is sufficiently close if the final figure is multiplied by ·004 to convert it into B.Th.U.

Recording Gas Analysis Apparatus for Flue Gases.—Automatic and partial analysis of flue gases furnishes a good check on the satisfactoriness of the stoking from the point of view of combustion. Various pieces of apparatus are advertised in the engineering journals. They depend on measurements of either (1) the volume or (2) the pressure of the flue gases before and after passing through an absorbent of CO_2, such as caustic potash solution. The percentage of CO_2 is indicated by a pointer or recorded on a roll of paper by means of a continuous curve.

The temperature of the flue gases can be recorded by means of a thermo-electric or resistance pyrometer placed in a suitable position and connected, as the case may be, with a "thread recorder," a recording galvanometer in which an inked thread is pressed on to a roll of paper by a pointer attached to the moving coil; or with a Callendar's recorder, an automatic and recording Wheatstone's bridge. Both these appliances are described in the publications of the Cambridge Scientific Instrument Company, who have specialised in this class of work.

CHAPTER III.

SAMPLING AND EXAMINATION OF LIQUID FUEL.

I. Sources of Liquid Fuel—Specifications and Sampling.

II. **Physical Examination.**—Flash Point—Fire Test—Specific Gravity—Refractive Index — Viscosity — Volatility — Distillation — **Chemical Examination**—Determination of Sulphur—Determination of Water—Qualitative Examination.

BEFORE considering the different methods used for testing liquid fuels, it is advisable to remember that there is a very large number of such liquids, many of which, although composed of bodies which are allied chemically, differ considerably as to their physical properties; these differences are frequently sufficiently great to render what would be regarded as a satisfactory fuel for a certain type of engine, a valueless material for engines of a different character.

For example, in what are known as petrol* engines it is necessary that the fuel shall be one which, under ordinary conditions of temperature, will be completely volatile in a current of air, and will thus readily produce an " air gas " for combustion in the cylinder.

There are other engines in which power is directly developed from the moderately heavy and less volatile liquids obtained by the distillation of crude petroleum, and finally we have the Diesel engine, in which so much interest has recently been manifested. This last-named example is capable of utilising the heaviest and least volatile oil fuels, and the late Dr. Diesel read a paper before the Institution of Mechanical Engineers in which he claimed that the following oils can be used with advantage:—(*a*) Mineral oils *freed from benzine* (*gas oils*); (*b*) lignite-tar oils; (*c*) fatty oils from vegetable and animal sources, such as earth-nut (arachis) oil, castor oil, fish oils, etc. In addition to these,

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* It should be mentioned that the word petrol was first used by a particular firm to designate a class of light spirit sold by them, and is not properly a generic name.

with the aid of special apparatus, pit coal-tar oil, water-gas and oil-gas tars, and tar from the vertical retorts used in coal-gas manufacture may be utilised.

It will be readily seen that there is a large number of available fuels, and an oil which has been found satisfactory in practice, from the engineers' point of view, should be carefully examined, and a specification prepared from the results of such examination, setting forth the requirements with which deliveries must comply.

The use of liquid fuels for steam-raising purposes is naturally greater in those countries in which oil is collected and refined. The residuum from the distillation of crude petroleum can be and is made use of in parts of the United States, Russia, and other oil-producing countries. In this country, where coal is cheap, the necessity for utilising waste-oil products has not always been sufficiently seriously considered; possibly this was partly due to the difficulty in obtaining satisfactory injector apparatus. The bulk of the heavy oils with which we have to deal in the United Kingdom are obtained during the carbonisation of coal, and the subsequent distillation of tar obtained therefrom. Dr. Diesel, in the paper mentioned, claimed that fuel oils, when used in the Diesel engine, yielded 2½ times more power than is obtained when used for raising steam for steam engines. Thermodynamical considerations, apart from the question of the suitability of such fuel for boiler furnaces, indicate that this is probable.

The significance of this statement, if borne out by subsequent experience, cannot be too strongly urged, as it affects the vital question of the husbanding of our national mineral wealth. Of course, steam is required for other purposes than power production, and in such cases it is probable that in this country coal would be the cheaper fuel to use.*

Alcohol as a Fuel.—Attention has been called recently to the largely increased consumption of the lighter hydrocarbons for motive purposes, and it is probable that in the comparatively near future it may be much more difficult than at present to supply the demand for this class of fuel. It is stated that alcohol is an excellent liquid fuel for the purposes of internal combustion engines, and no doubt can be entertained as to its suitability.

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* Mr. C. E. Strohmeyer, in his annual report (1912) to the Manchester Steam Users' Association, shows that the price of coal would have to rise to an enormous extent before it would be commercially profitable to burn crude oil in its stead.

As in all such cases the question resolves itself at the moment into one of price.

There is no doubt that when using hydrocarbon spirit we are utilising that which cannot be manufactured, whereas alcohol is prepared in very large quantities at the present day, and if necessary could be produced cheaply to a very much greater extent.

No serious attempt has yet been made to deal with this problem, but it is obvious that the use of a naturally occurring fuel cannot go on indefinitely, whereas the production of alcohol from starch in large quantities is possible, and would have an enormous industrial and economic significance.

I. Specifications and Sampling.—The following specifications will give an idea as to the conditions with which fuel oils for different purposes should comply.

For Petrol Engines.—Petrol, pure hydrocarbon spirit, of specific gravity not above 0·720, at 15·5° C.; 100 c.c. on distillation in a 3-bulb Ladenburg flask of 180 c.c. capacity to neck, should yield about 30 c.c. of distillate before the temperature reaches 80° C., and a total distillate of not less than 90 c.c. up to a temperature of 120° C., the process of distillation being carried out in about twenty minutes. The spirit must be completely volatile when exposed to the air in an open dish at a temperature not exceeding 70° F. The spirit must be in all respects suitable for use for motor purposes.

For Fuel Oil.—Specifications for the purchase of fuel oil, with directions for sampling it. I. C. Allen, U.S. Bureau of Mines, Technical Paper 3, 1911. The following specifications are recommended to the U.S. Government for the purchase of fuel oil (also, *J. S. C. I.*, Sept. 30, vol. xxx., 1911):—

General Specifications.—(1) In determining the award of a contract consideration will be given to the quality of the fuel offered by the bidders, as well as the price, and should it appear to be to the best interest of the Government to award a contract at a higher price than that named in the lowest bid or bids received, the contract will be so awarded. (2) Fuel oil should be either a natural homogeneous oil, or a homogeneous residue from a natural oil; if the latter, all constituents having a low flash point should have been removed by distillation; it should not be composed of a light oil and a heavy residue mixed in such proportions as to give the density required. (3) It should not have been distilled at a temperature high enough to burn it, nor at a temperature so high that flocks of carbonaceous matter began to separate.

(4) It should not flash below 60° C. (140° F.) in a closed Abel-Pensky or Pensky-Martens apparatus. (5) Its specific gravity should range from 0·85 to 0·96 at 15° C. (59° F.); the oil should be rejected if its specific gravity is above 0·97 at that temperature. (6) It should be mobile, free from solid or semi-solid bodies, and should flow readily at ordinary atmospheric temperatures, and under a head of 1 foot of oil, through a 4-inch pipe 10 feet in length. (7) It should not congeal nor become too sluggish to flow at a temperature of 0° C. (32° F.). (8) It should have a calorific value of not less than 10,000 calories per gramme (18,000 B.Th.U. per lb.); 10,250 calories (18,450 B.Th.U.) to be the standard. A bonus to be paid or a penalty deducted according to the method stated under section (21) as the fuel oil delivered is above or below this standard. (9) It should be rejected if it contains more than 2 per cent. of water. (10) It should be rejected if it contains more than 1 per cent. of sulphur. (11) It should not contain more than a trace of sand, clay, or dirt. (12) Each bidder must submit an accurate statement regarding the fuel oil he proposes to furnish. This statement should show (*a*) the commercial name of the oil; (*b*) the name or designation of the field from which the oil is obtained; (*c*) whether the oil is a crude oil, a refinery residue, or a distillate; (*d*) the name and location of the refinery, if the oil has been refined at all. (13) The fuel oil is to be delivered f.o.b. cars or vessel, according to the manner of shipment, at such places, at such times, and in such quantities as may be required during the fiscal year. (14) Should the contractor, for any reason, fail to comply with a written order to make delivery, the Government is at liberty to buy oil in the open market and charge against the contractor any excess of price, above the contract price, of the fuel oil so purchased.

Sampling.—(15) Deliveries of fuel oil will be sampled by a representative of the Government. Whenever such action is practicable, the oil will be sampled as it is being delivered. The final sample will be made from samples taken from as large a proportion of the delivery as practicable, in order that the final sample may truly represent the delivery. (16) The final sample will be sealed and forwarded to the Federal Bureau of Mines, Pittsburg, Pa., for analysis. (17) If the contractor so desire, permission will be given him, or his representative, to witness the sampling of the delivery and the preparation of the final sample. (18) The final sample will be analysed and tested immediately after its receipt in Pittsburg.

Causes for Rejection.—(19) A contract entered into under the terms of these specifications shall not be binding if, as the result of a practical test of reasonable duration, the fuel oil fails to give satisfactory results. (20) It is understood that the fuel oil delivered during the term of the contract shall be of the quality specified. The frequent or continued failure of the contractor to deliver oil of the specified quality will be considered sufficient cause for cancelling the contract.

Price and Payment.—Payment for deliveries will be made on the basis of the price named in the proposal for the fuel oil, corrected for variations in heating value, as shown by analysis, above or below the standard fixed by the contractor. This correction is a *pro rata* one, and the price is to be determined by the following formula :—

$$\frac{\text{Delivered calories per gramme (or B.Th.U. per lb.)} \times \text{contract price}}{\text{Standard calories per gramme (or B.T.U. per lb.)}}$$

$$= \text{price to be paid.}$$

Water that accumulates in the receiving tank will be drawn off and measured periodically. Proper deduction will be made by subtracting the weight of the water from the weight of the oil deliveries. The report also deals with the following points :—

Determination of Weight from Volume.—The observed specific gravity should be corrected by adding or subtracting 0·0006 for each 1° C. above or below the 15° C. The weight of 1 gallon in pounds is 8·3316 times the corrected specific gravity, or the weight of 1 cubic foot in pounds is 62·3245 times the corrected gravity.

Reporting Analyses of Fuel Oils.—The determinations to be made are the specific gravity at 15° C., the calorific value, the proportions of water, sulphur, and earthy matter, etc., the flash point, and the burning point.

Sampling Waggon Deliveries.—A pint dipper is filled with oil from the stream flowing from the waggon at regular intervals, twelve or more lots being taken. The sample should be labelled, so as to show the total bulk represented. A continuous sample may be run off from a cock on the underside of the delivery pipe. If a sample is required of oil delivered in separate lots over a period of time, proportional quantities of samples taken from the various deliveries may be mixed and stored in a tightly stoppered tinned drum, provided deliveries are of uniform quality. An iron drum should not be used, as it will absorb sulphur.

Sampling a Large Tank or Reservoir.—A dipperful should be taken from the bottom of the tank and examined for sediment. If a considerable amount of sediment is brought up, the oil should be rejected. If the oil has stood long enough to form strata of different densities, a sample should be taken by lowering an open iron pipe, 1 inch in diameter, vertically to the bottom of the tank, and then closing the bottom end by means of a conical wooden plug attached to a wire passing up through the tube. Similar samples should be taken from different parts of the tank, and mixed together. Alternatively, bottles full of oil may be taken from a number of different points in the tank.

Sampling from a Single Drum.—This may be done by dipping to the bottom with a glass tube, which is withdrawn while closed by the finger at the top end.

The directions for sampling given in the foregoing specification are those usually followed when dealing with liquids. They will probably be found adequate for most cases which may arise.

In an appendix to a paper on the Diesel engine by Dr. Diesel,* it is stated that the Swiss fuel testing laboratory at Zürich, under the direction of Professor Constam, groups "power oils" as follows:—

(1) *Normal Oils which can always be used*—

(*a*) Mineral oils freed from benzene (gas oils).	Hydrogen over 10 per cent. Calorific power over 10,000 cal. per kg. (18,000 B.Th.U. per lb.). No solid impurities.
(*b*) Lignite tar oils.	Hydrogen over 10 per cent. Calorific power over 9,700 cal. per kg. (17,460 B.Th.U. per lb.).
(*c*) Fat oils from vegetable or animal sources, such as earth-nut oil, castor oil, fish oils, etc.	Scarcely any researches have been made on these. Earth-nut oil has 11·8 per cent. hydrogen and calorific power 8,600 cal. per kg. (15,480 B.Th.U. per lb.).

(2) *Oils which can be used only with the Aid of Special Apparatus.*—(*a*) Pit coal-tar oil; (*b*) Vertical-oven, water-gas, and oil-gas tars, probably also coke-oven tars, the tests on which have not yet been completed.

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* *Proceedings Inst. of Mech. Engineers,* January-March, 1912.

General Characteristics.—Hydrogen not over 3 per cent.; amount of free carbon not over 3 per cent.; residue on coking not over 3 per cent.; calorific power not under 8,600 cal. per kg. (15,480 B.Th.U. per lb.).

(3) *Oils which cannot be used.*—Tars from horizontal or inclined retorts. It must not be understood that these will not be used in Diesel engines under special conditions; but, on the whole, the above classification is accurate in the present state of development of the Diesel engine.

It is evident that for estimating the value of power oils, not only the above qualities, but all their chemical and physical properties must be considered, which is only possible after a thorough investigation of each kind of oil.

In a second appendix, Dr. Diesel gives specifications of tar-oil suitable for Diesel engines (from the German Tar Production Trust at Essen-Ruhr.).

(1) Tar-oils should not contain more than a trace of constituents insoluble in xylol. The test on this is performed as follows:—25 grammes (0·88 oz. av.) of oil are mixed with 25 c.cm. (1·525 cub. in.) of xylol, shaken and filtered. The filter-paper, before being used, is dried and weighed, and after filtration has taken place it is thoroughly washed with hot xylol. After redrying, the weight should not be increased by more than 0·1 gramme.

(2) The water contents should not exceed 1 per cent. The testing of the water contents is made by the well-known xylol method.

(3) The residue of the coke should not exceed 3 per cent.

(4) When performing the boiling analysis, at least 60 per cent. by volume of the oil should be distilled on heating up to 300° C. (572° F.). The boiling and analysis should be carried out according to the rules laid down by the Trust.

(5) The minimum calorific power must not be less than 8,800 cal. per kg. For oils of less calorific value the purchaser has the right of deducting 2 per cent. of the net price of the delivered oil for each 100 cal. below this minimum.

(6) The flash-point, as determined in an open crucible by von Holde's method for lubricating oils, must not be below 65° C. (149° F.).

(7) The oil must be quite fluid at 15° C. (59° F.). The purchaser has not the right to reject oils on the ground that emulsions appear after five minutes' stirring when the oil is cooled to 8° C. (46° F.).

Purchasers should be urged to fit their oil-storing tanks and oil pipes with warming arrangements to redissolve emulsions caused by the temperature falling below 15° C.

(8) If emulsions have been caused by the cooling of the oils in the tank during transport, the purchaser must redissolve them by means of this apparatus.

Insoluble residues may be deducted from the weight of oil supplied.

Admiralty Specification for Oil Fuel (Cd. 7010).*—The following is the text of the Revised Admiralty Specification (1912) for oil fuel :—

Quality.—The oil fuel supplied shall consist of liquid hydrocarbons, and may be either (*a*) shale oil ; or (*b*) petroleum, as may be required ; or (*c*) a distillate or a residual product of petroleum ; and shall comply with the Admiralty requirements as regards flash point, fluidity at low temperatures, percentage of sulphur, presence of water, acidity, and freedom from impurities.

The flash point shall not be lower than 175° F. close test, Abel or Pensky-Martens. (In the case of oils of exceptionally low viscosity, such as distillate from shale, the flash point must not be less than 200° F.) The proportion of sulphur contained in the oil shall not exceed 3·00 per cent. The oil fuel supplied shall be as free as possible from acid, and in any case the quantity of acid must not exceed 0·05 per cent., calculated as oleic acid, when tested by shaking up the oil with distilled water, and determining by titration with deci-normal alkali the amount of acid extracted by the water, methyl-orange being used as indicator. The quantity of water delivered with the oil shall not exceed 0·5 per cent.

The viscosity of the oil supplied shall not exceed 2,000 seconds for an outflow of 50 cubic centimetres at a temperature of 32° F., as determined by Sir Boverton Redwood's standard viscometer (Admiralty type for testing oil fuel). (Pending settlement of this specification a viscosity of 1,000 seconds was provisionally adopted in 1912.) The oil supplied shall be free from earthy, carbonaceous, or fibrous matter, or other impurities which are likely to choke the burners. The oil shall, if required by the inspecting officer, be strained by being pumped on discharge from the tanks, or tank steamer, through filters of wire gauze having sixteen meshes to the inch.

The quality and kind of oil supplied shall be fully described.

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* *Journ. Soc. Chem. Ind.*, vol. xxxii., No. 17, p. 859.

The original source from which the oil has been obtained shall be stated in detail, as well as the treatment to which it has been subjected, and the place at which it has been treated. The ratio which the oil supplied bears to the original crude oil should also be stated as a percentage.

II. THE EXAMINATION OF LIQUID FUELS.

The Physical Examination usually comprises the determination of the flashing point, specific gravity, viscosity, volatility, and a distillation test; if the presence of oils other than those stipulated in the specification is suspected a determination of the refractive index may be of value. The chemical examination includes testing for the presence of mineral acids, alkali, and sulphur.

The examination depends very largely on the condition under which the fuel is to be used, and this will be clearly observed from the specifications already quoted. It would obviously be mere waste of time to determine the viscosity of a petrol which fulfilled the conditions mentioned in specification (1).

When dealing with the heavy viscous oils, such as are comprised under specifications (2) and (3), it is necessary to determine the amounts of water and dirt and other extraneous matters. With the lighter oils this is usually a matter of careful inspection.

The Flashing Point of a liquid is a purely arbitrary point, and can only be of value when a recognised apparatus, which can be standardised, is used in a prescribed manner. It is the temperature at which the inflammable vapours (which are evolved on gradually warming the oil) are present in sufficient quantity to give a slight explosion when brought into contact with a very small flame. In this country the "Abel" test was legalised in 1879, and the apparatus, together with the prescribed method for using it, is described in Schedule I. of the Petroleum Act, 1879.

It is necessary that the flashing points of all liquid fuels should be determined, not only to ascertain whether they conform to the conditions of the specification in this respect, but also for the purpose of enabling one to meet the requirements of the law. Should the flashing point be below 73° F. (as would undoubtedly be the case in the fuel oils used for petrol engines), provided the oil comes within the legal definition of petroleum, special precautions must be observed concerning the handling and storage of the liquid, such as will satisfy the authority responsible for the administration of the Petroleum Acts.

The Legal Definition of Petroleum (*Petroleum Acts*, 1871-1881).—"For the purposes of this Act, the term 'petroleum' includes any rock-oil, Rangoon oil, Burmah oil, oil made from petroleum, coal, schist, shale, peat, or other bituminous substance, and any products of petroleum, or any of the above-mentioned oils; and the term 'petroleum to which this Act applies' means such of the petroleum so defined as, when tested in manner set forth in Schedule One to this Act gives off an imflammable vapour at a temperature of less than seventy-three degrees of Fahrenheit's thermometer."

The Abel Test Apparatus (Fig. 14) and the method of using it are thus described in Schedule One to the Petroleum Act of 1879:—

"Specification of the test apparatus.

"The oil cup consists of a cylindrical vessel 2 inches diameter, $2\frac{2}{10}$ inches high (internal), with outward projecting rim $\frac{5}{10}$ inch wide, $\frac{3}{8}$ inch from the top, and $1\frac{7}{8}$ inch from the bottom of the cup. It is made of gun-metal or brass (17 B.W.G.) tinned inside. A bracket, consisting of a short stout piece of wire bent upwards and terminating in a point, is fixed to the inside of the cup to serve as a gauge. The distance of the point from the bottom of the cup is $1\frac{1}{2}$ inches. The cup is provided with a close-fitting overlapping cover made of brass (22 B.W.G.), which carries the thermometer and test lamp. The latter is suspended from two supports from the side by means of trunnions upon which it may be made to oscillate, it is provided with a spout, the mouth of which is $\frac{1}{16}$ of an inch in diameter. The socket which is to hold the thermometer is fixed at such an angle and its length is so adjusted that the bulb of the thermometer when inserted to its full depth shall be $1\frac{1}{2}$ inches below the centre of the lid.

"The cover is provided with three square holes,—one in the centre, $\frac{5}{10}$ inch by $\frac{4}{10}$ inch, and two smaller ones, $\frac{3}{10}$ inch by $\frac{2}{10}$ inch, close to the sides and opposite each other. These three holes may be closed and uncovered by means of a slide moving in grooves, and having perforations corresponding to those on the lid.

"In moving the slide so as to uncover the holes, the oscillating lamp is caught by a pin fixed in the slide, and tilted in such a way as to bring the end of the spout just below the surface of the lid. Upon the slide being pushed back so as to cover the holes, the lamp returns to its original position.

"Upon the cover in front of and in line with the mouth of the lamp is fixed a white bead, the dimensions of which represent the size of the test flame to be used.

"The bath or heating vessel consists of two flat-bottomed copper cylinders (24 B.W.G.), an inner one of 3 inches diameter and 2½ inches high and an outer one of 5½ inches diameter and 5¾ inches high; they are soldered to a circular copper plate (20 B.W.G.) perforated in the centre, which forms the top of the bath, in such a manner as to enclose the space between the two cylinders, but leaving access to the inner cylinder. The top of the bath projects both outwards and inwards about ⅜ inch; that is, its diameter is about $\frac{6}{8}$ inch greater than the body of

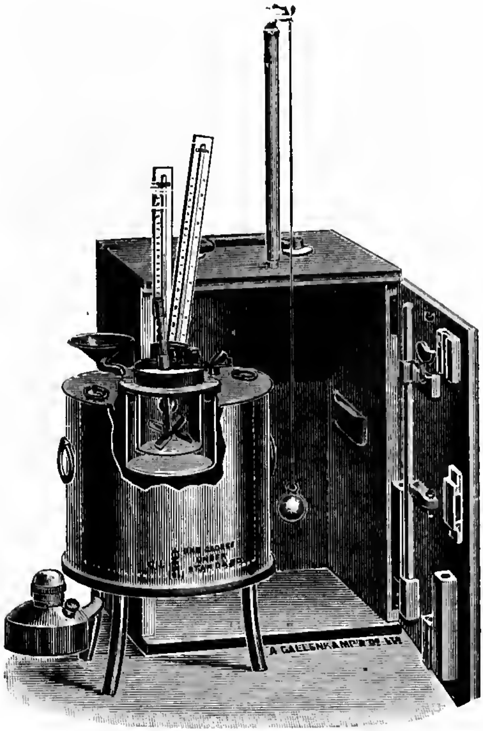

Fig. 14.—Abel flash-point apparatus.

the bath, while the diameter of the circular opening in the centre is about the same amount less than that of the inner copper cylinder. To the inner projection of the top is fastened, by six small screws, a flat ring of ebonite, the screws being sunk below the surface of the ebonite, to avoid metallic contact between the bath and the oil cup. The exact distance between the sides and bottom of the bath and of the oil lamp is ½ inch. A split socket similar to that on the cover of the oil cup, but set at a right angle allows a thermometer to be inserted into the space between the two cylinders. The bath is further provided with a funnel, an overflow pipe, and two loop handles.

"The bath rests upon a cast-iron tripod stand, to the ring of which is attached a copper cylinder or jacket (24 B.W.G.) flanged at the top, and of such dimensions that the bath, while firmly resting on the iron ring, just touches with its projecting top the inward-turned flange. The diameter of this outer jacket is 6½ inches. One of the three legs of the stand serves as a support for the spirit lamp attached to it by means of a small swing bracket. The distance of the wick holder from the bottom of the bath is 1 inch.

"Two thermometers are provided with the apparatus, the one for ascertaining the temperature of the bath, the other for determining the flashing point. The thermometer for ascertaining the temperature of the water has a long bulb and a space at the top. Its range is from about 90° F. to 190° F. The scale (in degrees of Fahrenheit) is marked on an ivory back fastened to the tube in the usual way. It is fitted with a metal collar, fitting the socket, and the part of the tube below the scale should have a length of about 3½ inches, measured from the lower end of the scale to the end of the bulb. The thermometer for ascertaining the temperature of the oil is fitted with collar and ivory scale in a similar manner to the one described. It has a round bulb, a space at the top, and ranges from about 55° F. to 150° F; it measures from end of ivory back to bulb, 2¼ inches.

"*Note.*—A model apparatus is deposited at the Weights and Measures Department of the Board of Trade."

Directions for applying the Flashing Test.

"1. The test apparatus is to be placed for use in a position where it is not exposed to currents of air or draughts.

"2. The heating vessel or water bath is filled by pouring water into the funnel until it begins to flow out at the spout of the vessel. The temperature of the water at the commencement of the test is to be 130° F., and this is attained in the first instance either by mixing hot and cold water in the bath, or in a vessel from which the bath is filled, until the thermometer which is provided for testing the temperature of the water gives the proper indication; or by heating the water with the spirit lamp (which is attached to the stand of the apparatus) until the required temperature is indicated.

"If the water has been heated too highly, it is easily reduced to 130° by pouring in cold water little by little (to replace a portion of the warm water) until the thermometer gives the proper reading.

"When a test has been completed, this water bath is again raised to 130° by placing the lamp underneath, and the result is readily obtained while the petroleum cup is being emptied, cooled, and refilled with a fresh sample to be tested. The lamp is then turned on its swivel from under the apparatus, and the next test is proceeded with.

"3. The test lamp is prepared for use by fitting it with a piece of flat plaited candle wick, and filling it with colza or rape oil up to the lower edge of the opening of the spout or wick tube. The lamp is trimmed so that when lighted, it gives a flame of about 0·15 inch diameter, and this size of flame, which is represented by the projecting white bead on the cover of the oil cup, is readily maintained by simple manipulation from time to time with a small wire trimmer.

"When gas is available it may be conveniently used in place of the little oil lamp, and for this purpose a test-flame arrangement for use with gas may be substituted for the lamp.

"4. The bath having been raised to the proper temperature, the oil to be tested is introduced into the petroleum cup, being poured in slowly until the level of the liquid just reaches the point of the gauge, which is fixed in the cup. In warm weather the temperature of the room in which the samples to be tested have been kept should be observed in the first instance, and if it exceeds 65°, the samples to be tested should be cooled down (to about 60°) by immersing the bottles containing them in cold water, or by any other convenient method. The lid of the cup, with the slide closed, is then put on, and the cup is placed into the bath or heating vessel. The thermometer in the lid of the cup has been adjusted so as to have its bulb just immersed in the liquid, and its position is not under any circumstances to be altered. When the cup has been placed in the proper position, the scale of the thermometer faces the operator.

"5. The test lamp is then placed in position upon the lid of the cup; the lead line or pendulum, which has been fixed in a convenient position in front of the operator, is set in motion, and the rise of the thermometer in the petroleum cup is watched. When the temperature has reached about 66° the operation of testing is to be commenced, the test flame being applied once for every rise of one degree in the following manner:—

"The slide is slowly drawn open while the pendulum performs three oscillations, and is closed during the fourth oscillation.

"*Note.*—If it is desired to employ the test apparatus to determine the flashing points of oils of very low volatility, the mode of proceeding is to be modified as follows:—

"The air chamber which surrounds the cup is filled with cold water to a depth of $1\frac{1}{2}$ inches, and the heating vessel or water bath is filled as usual, but also with cold water. The lamp is then placed under the apparatus and kept there during the entire operation. If a very heavy oil is being dealt with, the operation may be commenced with water previously heated to 120°, instead of with cold water.

"The pendulum described in (5) measures 24 inches from the point of suspension to the centre of gravity of the weight."

No departure may be made from the prescribed directions for applying the flashing test, and although it is known that a difference of 1 inch in the barometric pressure is sufficient to cause a difference of 2° F. in the flashing point, this point has no legal significance. Other sources of error have been investigated by J. H. Harker and W. F. Higgins,* who studied the following points:—(1) The influence of variations in the method of testing (*a*) the frequency of application of the test flame, (*b*) variations in the time of opening the slide, (*c*) variations in the water-bath temperature, (*d*) variations in the depth of immersion of the thermometer; (2) the temperature distribution in the oil cup of the various forms of apparatus; (3) the heat from the test flame, differences of $\frac{1}{2}$° F. may occur even in the most careful work, more especially in the apparatus provided with the oil test flame; (4) the difference between the flash points determined with the different forms of apparatus. These are approximately constant at all temperatures; the German form gives results

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* *Nat. Phys. Lab. Coll. Researches*, vol. viii., pp. 19-39.

about 3·7° F. and the Colonial form 1·1° F. higher than the Abel. The oil test flame reads about ½° F. higher than the gas flame. (5) They emphasise the fact that the flash point of a liquid, as ordinarily determined, is an empirical constant which is largely a function of the particular apparatus used. The effect of thermometric lag was also investigated by them.

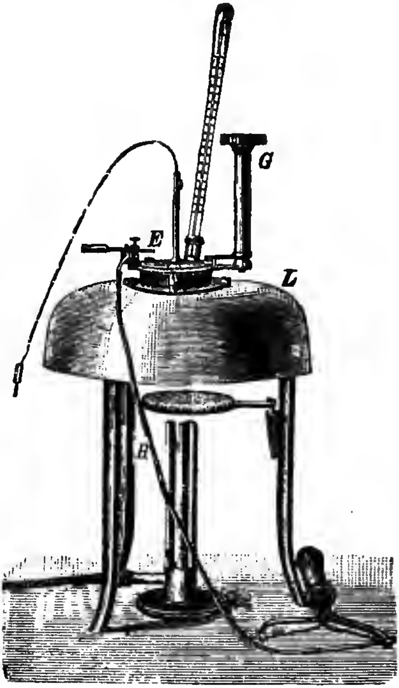

Fig. 15.—Pensky-Martens' flash-point apparatus.

The German Government, as the result of an investigation on their behalf, adopted the Abel instrument as the best for determining the flashing point. The method of applying the test flame, on account of the personal error liable to be introduced, was altered, and Pensky designed a clock-work arrangement to be fitted to the apparatus, thus ensuring an automatic method of opening the slide and at the same time applying the test flame. This apparatus is known as the Abel-Pensky instrument.

The Flashing Point of Heavy Oils is best determined in an instrument such as the Pensky-Martens tester, which is largely used for this purpose. It may be briefly described as consisting of an oil cup fitted with a cap somewhat similar to that of the Abel instrument, in so far that it carries a gas jet, a socket for a thermometer, and is provided with three holes, which are opened at the same time that the gas jet is depressed. In addition a stirrer with two sets of vanes is fitted, one set of which serves to ensure the oil being thoroughly stirred throughout the determination, the other set working in the vapour above the oil. The stirrer is worked by means of a small flexible shaft. The heating arrangement consists of a cast-iron air bath, which is heated by a Bunsen burner, and arrangements are made so that the oil cup does not come into contact with the air bath.

The Fire Test or Firing Point is the temperature at which the oil takes fire and continues to burn. It may be determined by heating the oil in a cup (usually one about the size of the oil cup used in the flashing point apparatus is taken) over a small Bunsen burner, and applying a flame, say every 5°, until the oil takes fire. A thermometer which is suspended from above the cup so that its bulb is well covered by the liquid may be utilised as a stirrer, and when the firing occurs the temperature is readily observed.

The Specific Gravity or density may be determined by means of a hydrometer, the Westphal balance, or a pyknometer, such as the ordinary specific gravity bottle, or the Sprengel tube.

The determination by means of a hydrometer is not altogether satisfactory, as it is necessary to have a large volume of liquid, and in addition there is always a certain amount of trouble in reading the scale division, owing to the meniscus of the oil and the capillary attraction of the stem of the hydrometer. However the instrument is used, and if it be standardised against liquids, the specific gravity of which have been determined by a pyknometer, most of the objections to its use are removed.

The Westphal balance affords a convenient and accurate means of determining density. The instrument consists of a beam divided into ten equal parts. At the extremity of the beam a glass plummet is suspended, and the apparatus is adjusted, until the largest rider supplied when attached to the hook at the last division maintains equilibrium when the plummet is completely immersed in water at 60° F.

The jar, in which the liquid to be tested is placed, is then filled with the oil, also at a temperature of 60° F., and, by means of the different riders, equilibrium is again restored. By noting the position of the riders, the density may be easily read.

With the ordinary specific-gravity bottle the method of procedure is to weigh the clean dry bottle, then fill it with boiled distilled water at 15·5° C. (60° F.), and again weigh. This operation should be repeated two or three times. The difference in weight gives the weight of water at a known temperature required to fill the bottle.

After thoroughly drying the bottle, it is filled with the sample under examination at the same temperature (60° F.), and the weight again noted. The difference in weight gives the weight of oil, and the figure divided by the weight of water previously ascertained gives the relative density of the oil at 60° F. Most specific-gravity bottles have the capacity marked on them, but such figures are only approximate, and should on no account be taken as more than a rough indication of the weight of water contained by the bottle when filled.

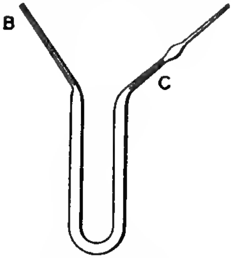

Fig. 16.—Perkin's Sprengel tube.

The Sprengel tube is unquestionably the best and most accurate form of apparatus for determining specific gravities, and it has the following advantages:—It can easily be made in the laboratory; small quantities of the liquid under examination may be employed; it is easy to manipulate, and is very convenient if it be desired to determine the gravity at a higher temperature than that usually employed.

A useful form of the apparatus, described by the late Sir William Perkin,* consists of a small U-tube, the ends of which have been drawn out and bent, as shown in Fig. 16. The tube is filled with the liquid to be tested by drawing the oil in at one end and by suction at the other, until the tube is full. The whole is then placed in a vessel of water until the oil has acquired the temperature of the latter. By means of a piece of absorbent paper applied at the end B the excess of oil is withdrawn until the

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* *Trans. Chem. Soc.*, vol. xlv., p. 444.

meniscus of the liquid in the other limb coincides with the scratch mark C. The small glass caps, which are only necessary when volatile liquids are to be weighed, are placed over the open ends of the tubes, the whole is removed from the water, carefully wiped from adhering water, and weighed. A piece of aluminium wire with two hooks is a convenient device for lifting the tube from the beaker, and also for suspending it during the weighing. The capacity of the tube is previously ascertained by weighing it full of distilled water at 60° F., or at known temperatures near, above, and below this, and the calculation of the specific gravity is made as with the bottle.

The specific gravity of liquids is usually determined at a temperature of 60° F., referred to water at the same temperature, but it is not always an easy matter to arrange this; of course, it may be done by either warming or cooling the liquid (as circumstances require), but it may prove a tedious business and occupy some time in doing. In such cases the coefficient of expansion of the oil may be made use of, and a correction added or subtracted to the observed gravity, in order to return the gravity at 60° F. In the case of the hydrocarbon oils, the coefficient of expansion varies with the specific gravity, as may be seen from Table V. from Allen's *Commercial Organic Analysis.*

TABLE V.—Expansion Coefficient for Oils.

Specific Gravity at 15° C.	Expansion Coefficient for 1° C.
Under 0·700	·00090
·700-·750	·00085
·750-·800	·00080
·800-·815	·00070
Over ·815	·00065

This table may be used when the temperature varies several degrees (say up to 10°) on either side of 15° C., if the oil under examination is a hydrocarbon oil; it should be clearly understood that for exact purposes the specific gravity at 15° C. should be determined directly, either by cooling or warming the sample until the standard temperature is reached, and then proceeding as already described. If it is desired, two determinations at temperatures respectively above and below, but near to 60° F., may be made, and the results corrected to 60° by calculation.

When dealing with very viscous oils we have found that it is a difficult matter to transfer such liquids to gravity bottles, and other apparatus having finely drawn tubes. A method which gives good results is to fill a stout glass bottle of about 50 c.c. capacity having a wide neck (Fig. 17), the top edge of which is ground. A ground-glass disc is then pushed on sideways, and the weighings performed as with an ordinary specific-gravity bottle. The temperature of the oil is noted before pouring into the bottle, and the necessary correction for temperature is made. The method is rapid and sufficiently accurate, the results agreeing with those made in the ordinary gravity bottle.

The Viscosity of a liquid may be defined as the measurement of the amount of internal friction occurring between the particles of the liquid. It varies in some cases considerably for comparatively small differences of temperature. The following definition gives a better idea of what viscosity really is :—

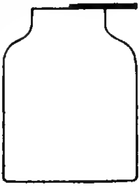

Fig. 17.
Merry's bottle.

If two parallel planes are at a unit distance apart in a fluid, and one of them is moving in its own plane with unit velocity relatively to the other plane, then the tangential force exerted per unit area on each of the planes is equal to the viscosity.

For the capillary-tube method of determining viscosities, Poiseuille's formula is

$$\text{Viscosity } \eta = \frac{\pi p r^4 t}{8 l v},$$

where p = pressure difference between the two ends of the tube.
r = radius of the tube, l = length of tube.
v = the volume of liquid delivered in time t.

Ostwald's Capillary Pipette (for description, see Ostwald-Luther, *Physikalische Chemische Messungen*, p. 260) is perhaps the most scientific form of apparatus for the determination of this value.

It is not used, however, for technical purposes.

By this method the time taken for the liquid to flow from the mark c to d (Fig. 18) is noted ; the capillary tube should be from 10 to 12 cm. long, and the volume of the bulb sufficiently large for the time of outflow to be at least 100 seconds.

The "viscosity" (as known in commerce) of a liquid is usually determined by noting the time required for a given volume to flow from a jet fixed in the bottom of a cup containing the liquid. The test is a most important one in connection with the examination of lubricating oils, and although its use in connection with the fuel oils may not be generally indicated, yet in the case of the heavy oils, such as described in specification (3), it would certainly give more definite information than the rather vague "should flow readily at ordinary atmospheric temperatures, and under a head of 1 foot of oil through a 4-inch pipe, 10 feet in length." We do not suggest that the clause quoted is not a sound one, but it would be better, after having ascertained the viscosity of an oil which passed the conditions quoted above, to give the additional information resulting from the determination.

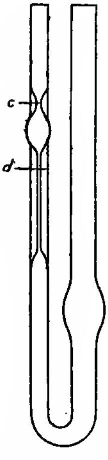

Fig. 18.—Ostwald's capillary pipette.

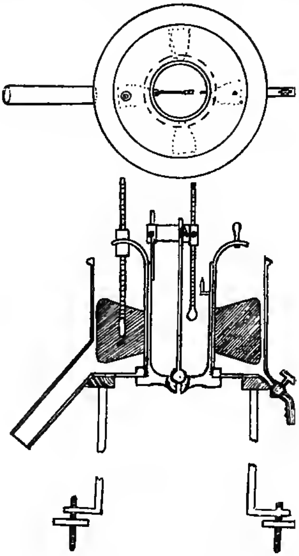

Fig. 19.—Redwood's viscometer.

Redwood's Viscometer * (Fig. 19) is the pattern usually adopted in this country. It consists of a silvered copper oil cylinder about $1\frac{7}{8}$ inches in diameter and $3\frac{1}{2}$ inches deep, furnished with an agate

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* *Journ. Soc. Chem. Ind.*, vol. v., p. 158.

jet fitted into a slightly conical metal seating. The cylinder is fixed in a brazed copper water bath provided with a copper heating tube projecting at an angle of 45° from the side near the bottom, as well as with a revolving agitator carrying a curved shield to prevent splashing, and a thermometer to indicate the temperature of the liquid in the bath. The oil cylinder has a stopper consisting of a small brass sphere which rests in a hemispherical cavity in the agate jet. The sphere is attached to a wire by means of which it is raised and suspended from a standard which supports a thermometer in the oil. Inside the oil cylinder, and at a short distance from the top, is fixed a small bracket terminating in an upturned point, which serves as a gauge of the height to which the cylinder is filled. The instrument is supported on a tripod stand furnished with levelling screws. Great care is taken in the construction of the agate jets to secure uniformity, and any small differences in the rate of flow are corrected by slightly altering the position of the bracket in the oil cylinder. Notwithstanding this, the agreement between different instruments is not altogether as satisfactory as could be desired.

Method of Using the Apparatus.—The bath is filled with a suitable liquid to a height corresponding with the bracket in the oil cylinder. Water may be used for temperatures up to 200° F., and a heavy mineral oil for higher temperatures. The liquid being at the required temperature, the oil to be tested, which may previously be brought to the same temperature, is poured into the inner cylinder until its level just reaches the point of the gauge. A narrow-necked flask, holding 50 c.c. to a point marked on the neck, is placed beneath the jet in a vessel containing a liquid of the same temperature as the oil. The ball valve is then raised, a stop watch at the same time started, and the number of seconds occupied by the outflow of 50 c.c. noted.*

The apparatus of Dr. Engler is the recognised form of testing apparatus in Germany, and the time taken for the outflow of the oil is compared with the time taken to collect 200 c.c. of water at 20° C. The viscosity of the oil is represented by the figure obtained by dividing the former by the latter result.

The apparatus consists, as in the Redwood instrument, of an inner cup and a heating bath, fitted with thermometers and a wooden plug for closing the orifice, through which the liquid flows into the measuring flask. Both forms of apparatus require

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* In practice it is not usual to stand the flask in a bath as described; the omission to do so has no appreciable effect on the results obtained.

a large volume of liquid, and neither is in a strict sense a viscometer.

The Volatility is usually determined by exposing a known weight of the liquid in a flat metal dish of about 2½ inches diameter to the temperature of the room, and weighing at regular interval until no further loss occurs. In the case of the light hydrocarbons the residue should be *nil.* With heavy oils the exposure is usually made at the temperature of the steam oven, and the *loss* in weight should not exceed a few tenths of 1 per cent.

In the case of oils occupying intermediate positions between these two classes, the volatility test is not of much importance.

The Distillation of fuel oils affords valuable information as to their probable composition and behaviour; it enables one, in the case of a hydrocarbon oil, to decide whether the oil is a normal distillate obtained by the distillation of the crude oil, or a blended product prepared by the admixture of light and heavy fractions.

The method and the apparatus used for the distillation should be specified, as only by so doing can comparable results be obtained; thus in the specification for petrol previously quoted, the volume of oil distilled, the form and capacity of the flask, and the time taken for distillation for a certain range of temperatures are specified. In the specification for the tar oil suitable for use in the Diesel engine 60 per cent. by volume of the oil should distil up to a temperature of 300° C.

Engler's method is largely used for the fractional distillation of oils, and the following is a description of the apparatus employed. The distilling vessel is of the form usually known as a Wurtz flask, 6½ cm. in diameter, with a cylindrical neck 1·6 cm. in internal diameter and 15 cm. long. From the side of the neck a vapour tube, 10 cm. in length, extends at an angle of 75° downwards to the condenser. The junction of the vapour tube with the neck of the flask should be 9 cm. above the surface of the oil when the flask contains its charge of 100 c.c. of the oil. *The observance of the prescribed dimensions is considered essential to the attainment of uniformity of results.* A thermometer is fixed in the cork inserted in the mouth of the flask, so that the top of the bulb is on a level with the vapour tube. 100 c.c. of the oil is introduced into the flask by means of a pipette, and heat is applied by means of a Bunsen burner. At first, wire gauze is interposed between the burner and the flask, but afterwards the naked flame is employed, the heat being so regulated that from 2 to 2½ c.c. of distillate passes over per minute. In the specification for petrol the capacity and general form of the distilling flask only are given, but as we are dealing with a comparatively limited fraction of the petroleum products, and as the apparatus is a "stock" pattern, this may be deemed sufficient.

Another method of distillation is to distil from a bolt-head flask fitted with a Young's four-pear stillhead. This last-named method is, in our opinion, the most suitable, and should prove of service in preparing specifications where ranges of distillation are required to be given.

When dealing with oils of a heavy and viscous nature, it is important to ascertain their behaviour when subjected to a low temperature, and it will have been noticed that in Specification (3) a clause is inserted that the oil should not be too sluggish to flow at 0° C. This is best determined by immersing a test tube containing some of the oil, in a mixture of ice and salt for about an hour. On removing the tube and inclining it, the oil should not show signs of congelation, and should flow along the inclined tube.

The foregoing tests comprise all that is necessary for the physical examination of liquid fuels, but it should be borne in mind that it is not necessary to apply all the tests to all fuel oils; the conditions under which the latter are to be used must be taken into consideration, and such tests made as will ensure the procuring of the material required.

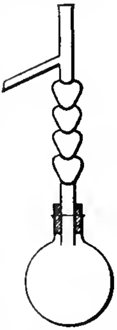

Fig. 20. Young's four-pear stillhead with flask.

Chemical Examination.—The chemical examination of liquids includes the testing for the presence of traces of alkalies and of mineral acids; the determination of sulphur and, in the case of the heavy dark-coloured oils, the determination of water and mineral matter (such as sand, dirt, earthy matter, etc.). The last two named substances are not likely to be present in the lighter and faintly coloured oils; if present, careful inspection would enable one to decide whether determinations of them are necessary.

The presence of alkalies and mineral acids is readily detected by agitating about 100 c.c. of the liquid with an equal volume of distilled water in a separating funnel. After standing for a short time, the lower aqueous layer is drawn off, and the behaviour of one portion is noted, when a few drops of an alcoholic solution of phenolphthalein are added to it. A pink colouration indicates the presence of free alkalies. To another portion a drop or two of methyl-orange solution is added. A pink colouration in this case would indicate the presence of mineral acids.

Sulphur.—The determination of sulphur in any liquid fuel is best accomplished by the combustion of a known weight of the substance in a bomb calorimeter; the details of this process will, however, be fully described in the chapter dealing with the determination of the calorific power of fuels by means of the bomb calorimeter. Other methods are available, and include the method of Carius, combustion in a current of oxygen, etc. We do not propose to give these as the figures obtained cannot be relied upon, owing to the difficulty experienced in completely oxidising the sulphur present, especially in the case of the more volatile liquids.

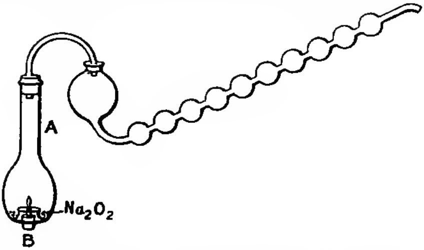

Fig. 21.—J. M'Connell-Sanders sulphur apparatus.

As an alternative method to that of combustion in the bomb we prefer to utilise the apparatus prescribed by the Metropolitan Gas Referees for the estimation of sulphur in coal gas. The results obtained are satisfactory, and the method is perhaps preferable to any other in those cases where the amount of sulphur present is extremely small, as one can burn as much as 10 grammes (or more) of the liquid under examination; this would necessitate ten combustions of 1 gramme lots if the bomb were employed, and would obviously be a somewhat laborious process.

The apparatus, as used for gas, is shown in Fig. 13. The only difference to be noted is that the gas burner is replaced by a small spirit lamp in which the oil is burned.

A known weight of the liquid to be tested is placed in the lamp; if not sufficiently volatile it is mixed with alcohol and ether, the glass balls are moistened with water, and the apparatus set up as shown in the figure, care being taken that the rubber joints are tight. When the combustion is completed the condenser is thoroughly washed out with distilled water, this operation being performed by disconnecting the cork carrying the chimney tube and pouring the water in at the top of the condenser. The rinsings, together with the condensed products, are acidified with HCl, boiled for several minutes, and an excess of barium chloride added, drop by drop from a pipette, to the boiling liquid. The boiling is continued until the supernatant liquid shows signs of clearing, when the beaker is removed from the flame, and allowed to stand for about thirty minutes. The precipitated barium sulphate is filtered, washed with hot water until free from chlorides, and then ignited in a weighed dish.

$$\frac{\text{Wt. of } BaSO_4 \times 13{\cdot}74}{\text{Wt. of sample taken}} = \text{per cent. of sulphur in the fuel.}$$

A paper by James M'Connell-Sanders * on the "Determination of Sulphur in Petroleum" gives some new modifications of methods already in vogue.

One, which is a modification of that just described, consists in burning a known weight of the oil in a platinum crucible which has been packed with recently ignited asbestos. The crucible is covered with a Rose's crucible lid, through the central hole of which a piece of pipe-clay tube carrying an asbestos wick is placed, the wick being embedded in the asbestos packing of the crucible. The crucible is supported beneath a flask which has been manipulated in the flame, so as to provide a gallery, in which sodium peroxide with a small amount of anhydrous cobalt chloride is placed. The neck of the flask is fitted with a cork (covered with tin foil), carrying a bent tube, and is connected with a Meyer absorption apparatus, three or four bulbs of which are filled with water in which a little sodium peroxide has been placed. The free end of the absorption apparatus is connected to a pump, and a free current of air is drawn through the apparatus, after having lighted the lamp. When nearly all the oil has been burned, by means of a small spirit flame, the crucible is gently heated at first, and finally to low redness, to

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* *Trans. of the Chem. Soc.*, March, 1912.

burn off any heavy residue. When the combustion is concluded, the whole of the contents of chimney, bulbs, etc., are transferred to a beaker, the apparatus is rinsed out with distilled water, and the precipitation and subsequent treatment of the barium sulphate is carried out, as previously described.

The percentage of solid impurities may be determined by diluting a known weight of the sample with petroleum spirit, filtering the suspended matter on a weighed filter, and washing the latter repeatedly with fresh portions of spirit until free from oil. The filter is then dried and weighed, the increase in weight being due to the solid impurities. If sufficient in amount, a qualitative examination should be made.

Note.—In all operations involving the use of petroleum spirit the greatest care must be exercised to avoid the proximity of naked lights; in fact, all such work should be conducted in a room free, for the time being, from such if possible.

Water.—The determination of water in a heavy viscous liquid fuel is a difficult matter, as the method of heating a known weight in the steam oven is open to the objection that the resulting loss may have been due to the volatilisation of any light oil present. On the other hand, the method of diluting with gasoline and allowing the water to separate is likely to give low results owing to the non-separation of all the water present.

The following abstract of recent work on this subject is taken from the *Journ. Soc. Chem. Ind.*, vol. xxxi., pp. 862-863, 1912 :—

"Methods for the Determination of Water in Petroleum and its Products." I. C. Allen and W. A. Jacobs. *Eighth Int. Cong. Appl. Chem.*, 1912, Sect. Vc. Orig. Comm., x., pp. 17-23.

Methods depending on the loss of weight on heating are approximate, and are only applicable to heavy oils and greases. Dilution with gasoline and separation of the water from the diluted oil by gravity, or by a centrifuge, is an approximate method applicable to thin oils. Other approximate methods are by comparing the colour with that of standard mixtures of oil and water, and by agitating the oil, diluted with petroleum spirit with $\frac{N}{10}$ acid, and then titrating a portion of the separated water. Four accurate methods are described.

1. *Treatment with Calcium Carbide.*—17·24 grammes of the sample are placed in a 250 c.c. separating funnel, and a 100 c.c. separating funnel containing 10 grammes of powdered calcium carbide, is fitted to the neck of the first funnel. The neck of the second funnel is fitted with a stopcock. The apparatus is brought

to a standard temperature in a water bath, the cocks are then closed, and the carbide mixed with the petroleum. The apparatus is again brought to the standard temperature, and is connected with a gas burette, which measures the volume of gas generated. One gramme of water generates 580 c.c. of acetylene, and the oil absorbs, on the average, 1·1 times its volume of acetylene.

2. *Treatment with Sodium.*—The method is the same as with calcium carbide, about 2 grammes of finely cut sodium being used for 1 gramme of water. This method is very accurate, since hydrogen is insoluble in the oil.

3. *Distillation with a Non-miscible Liquid.*—100 grammes of the oil are mixed with 200 grammes of toluene, benzene, or xylene, and distilled. The water separating in the distillate is measured. The results are accurate to within 0·033 gramme of water per 100 c.c. of distillate.

4. *Direct Distillation of the Water.*—200 grammes of the oil are distilled in the ordinary way, and the water in the fractions between 100° and 150° C. is separated and weighed. The condenser should be cooled to 2° C. Bumping is prevented by passing a current of dry carbon dioxide through the oil. The method is accurate within 0·03 per cent.

Emulsions may be subjected to the action of a high tension electric current (2,200 volts), in order to cause water to separate. The emulsion is placed in a glass cylinder containing a roll of copper gauze for one terminal and a central copper wire or rod for the second terminal. The water in the emulsion is reduced to 0·5 per cent. in half-an-hour.

Qualitative Examination.—It is possible that occasion may arise when a qualitative examination of a liquid fuel would be of value, although the necessity of such examination, we admit, is a remote one. The following extracts are from a paper read by Mr. E. T. Shelbourn and the authors before the Society of Public Analysts, January, 1912 :—

It is obvious that in many cases some of the processes suggested could be omitted or modified, and that at various stages much useful information will be given by the determination of such physical properties as refractive index, boiling point, and specific gravity, and by the consideration of the relation of these constants to one another. The odour and the nature of the flash given by liquids will often furnish useful qualitative information.

A liquid, which on agitation with water is found to be wholly miscible with it, cannot contain any appreciable quantity of the hydrocarbons, which are the main constituents of petroleum as known to the law. If any loss of volume occurs, owing to the solution of a portion of the sample, it should be washed with further quantities of water until all soluble constituents (alcohol, acetone, etc.) are removed. These washings, or the water coming over with the steam distillate, may be examined by determining the initial boiling point of the liquid and the properties of the first portion of the distillate.

Viscous liquids which obviously contain fixed oils or solids in solution or suspension can be distilled either alone at ordinary or reduced pressure or with steam, in order to obtain a suitable liquid for working on.

Whether the sample has been distilled with steam or alone, or only washed with water, the treatment with sodium bisulphite and calcium chloride to remove acetone and alcohol respectively should be carried out on the sample or the distillate. Only hydrocarbons are now likely to be present. The hydrocarbons may be terpenes, paraffins and cycloparaffins, and aromatic hydrocarbons. Terpenes may be removed by Armstrong's method,* which has been shown by one of us to be applicable to mixtures of terpenes with both aliphatic and aromatic hydrocarbons.† The remaining liquid can only contain paraffins and cycloparaffins, and homologues of benzene.

From a mixture containing possibly both aromatic and aliphatic hydrocarbons it is easy to remove aromatic hydrocarbons either by *careful* nitration followed by fractional distillation or by sulphonation. It must be borne in mind that if terpenes have been found in the liquid, the presence of aromatic hydrocarbons to the extent of from 5 to 12 per cent. of the terpenes found is probable, owing to the cymene obtained when turpentines are polymerised. This amount should be deducted from any aromatic hydrocarbons which may be found.

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* *Journ. Soc. Chem. Ind.*, vol. i., p. 480, 1882.

† Coste, *Analyst*, vol. xxxv., p. 438, 1910; Coste and Nash, *ibid.*, vol. xxxvi., p. 207; 1911.

CHAPTER IV.

SAMPLING AND EXAMINATION OF SOLID FUEL.

I. SAMPLING OF SOLID FUEL OR COAL.—General Directions for Sampling—Treatment of Laboratory Samples.

II. ANALYTICAL EXAMINATION OF COAL—(*a*) **Proximate Analysis of Coal**—Determination of Water—Appliances for drying Coal—Determination of Volatile Combustible Matter in Coal—Determination of Fixed Carbon in Coal—Coking Tests—Gas-making Tests—Determination of Ash, etc., in Coal. Extraction of Coal by Solvents—Carbonisation of Coal at Regulated Temperatures. (*b*) **Ultimate Analysis of Coal**—Determination of Carbon, Hydrogen, Nitrogen, and Sulphur.

III. CLASSIFICATION OF COALS ON RESULTS OF ANALYSIS—Examination of Coke, Briquettes, Peat, etc.

I. THE SAMPLING OF SOLID FUEL OR COAL.

THE sampling of solid fuels is a matter of the utmost importance, and should be conducted with the greatest care and intelligence, as the results of the subsequent examination of the sample often refer to very large consignments of fuel, in some cases as much as 1,000 tons. The sample, as received in the laboratory, does not exceed, as a rule, 10 lbs. in weight, and the preparation of this small amount for examination is not a difficult matter; the important point is that the large sample representing the cargo, from which the laboratory sample has been withdrawn, shall, so far as is possible, accurately represent the average composition of the consignment. In the case of coal of fairly uniform size this is a comparatively simple matter, but in other cases where the size of the coal ranges from large lumps down to small coal, it is essential that the sampling shall be conducted by an experienced sampler, so as to ensure a due proportion of the different sized lumps being present in the sample. The importance of this point may be seen by referring to the following table, in which it is shown that coal from the same vein varies in composition with the size of the coal.

TABLE VI.*—PERCENTAGE OF ASH IN COAL FROM THE SAME VEIN, BUT OF DIFFERENT FINENESS.

Size of Coal.			Moisture.	Ash.
	Through.	Over.		
Egg, .	2·5	1·75	1·72	5·66
Stove, . .	1·75	1·25	1·43	10·17
Chestnut, ...	1·25	0·75	1·73	12·67
Pea, . . .	0·75	0·50	1·76	14·66
Buckwheat,	0·50	0·25	1·69	16·62

It will be observed that the percentage of ash increases as the size of the coal diminishes.

We have had occasion to examine samples of coal of varying sizes, although obtained from the same seam, and have always found an increase in the amount of ash as the size of the coal diminished. This is due to the fact that during the washing of the coal the extraneous earthy matter will naturally be washed off the larger coal and aggregate with the finer portions.

The report of the International Committee on Analysis to the Eighth International Congress of Applied Chemistry, 1912, includes a comprehensive chapter on the subject of sampling, and the following extracts are taken therefrom :—

" General Directions for Sampling.

" **Need of Experience and Caution.**—Persons who have had no experience in taking samples are liable to select a sample better than the average run of the coal. Occasionally a lump of coal is broken and shipped to the laboratory in a cloth sack, which allows the moisture to dry out ; moreover, the lump selected is usually free from layers of slate and impurities, and of course then represents the best coal in the lot rather than the average, and its analysis will show a higher value than the coal delivered. Especial care should be exercised to note the proportion of slate and other foreign substances, in order that such impurities may be included in the sample in the same proportion. Experience and good judgment on the part of the sampler are necessary to insure the collection of a representative sample ; and it is well to remember that as the larger lumps of coal roll down and

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* Stillman, *Engineering Chemistry*, p. 25.

collect near the bottom of a pile or load a sample taken entirely from near the floor would not fairly represent the whole.

" **Loss of Moisture in Samples.**—In spite of every precaution taken to prevent loss of moisture during the collection, preparation, and analyses of samples, it is certain that loss of moisture may occur, whereby the heat value of the coal as shown by analysis of the sample is greater than that of the coal from which the sample was taken. It is important to the purchaser and fair to the dealer that the quality should be determined on the coal 'as received.' In the interest of equity, therefore, the suggestions that follow are presented for the guidance of those who wish to send samples to a laboratory for analysis.

" **Waggonload Deliveries.**—Samples taken from coal delivered at a department building should consist of a shovelful of coal taken from each waggonload, or from each third or fifth load, the number of samples taken depending on the loads delivered. It is important to obtain representative portions of coal from every part of the delivery, so that the samples will show the quality of the delivery or order as a whole. The sample should contain about the same proportion of lump and fine coal that is contained in the coal as delivered.

" If the quantity delivered is 100 tons or more, at least two samples should be taken, one representing the earlier and the other the late delivery. The average of two or more analyses will represent more accurately the quality of the coal than a single analysis, because it is difficult to preserve the character of the large sample in reducing it to the small sample required for laboratory use.

" **Cargo Deliveries.**—In determining definitely the number of samples to be taken to represent different quantities delivered many variable factors must be considered. For cargoes of 4,000 to 6,000 tons the approved method is to take a sample of about 65 lbs. from every third railroad car when unloaded; three such samples, representing nine cars, are mixed and reduced by quartering to the regular 2-lb. sample. By this procedure 8 to 14 samples are obtained for the cargo. An analysis representing the whole cargo is obtained by averaging the results of analyses. It is impracticable to take a single large sample to be fairly representative and reduce it to a 2-lb. sample for laboratory treatment, for the analysis of a single sample would probably not correctly represent the quality of the whole of a large cargo.

“ **Stowage and quartering down.**—A gross sample should, when taken, be immediately placed in a metal receptacle having a tight-fitting cover and a first-class lock, and when samples are being quartered down each receptacle should be securely locked and the key held by a responsible employee. The receptacle should be placed in a comparatively cool place to minimise loss of moisture from the sample ; and for the same reason the process of quartering down and preparing samples for shipment to the chemical laboratory should be carried on as rapidly as possible. This process, briefly described, is as follows :—

“ The contents of the receptacle or receptacles are emptied in a clean, dry space, preferably on a sheet-iron plate of suitable dimensions, so located as to prevent admixture of foreign matter with the sample during its preparation. All the lumps are then broken by a maul or sledge until they will pass through a half-inch mesh. The mass is then thoroughly mixed, formed in a conical pile, and equally quartered by means of a shovel or board. Two opposite sections are next rejected and the remaining sections are mixed. The pile is then reformed and opposite quarters are discarded as before. This process is continued until only about 2 lbs. remain. This final sample is immediately placed in a suitable receptacle and is sealed air tight.

“ The 2-lb. sample is next reduced to 20-mesh fineness in a roll crusher, and is then thoroughly mixed. A 2-oz. portion is withdrawn and placed in a rubber-stoppered bottle preparatory to determining its content of moisture. The remainder is passed through riffles and reduced in quantity to about 2 ozs. This 2-oz. sample is further reduced in fineness on a bucking board until all its particles will pass through a 60-mesh screen. It is then placed in a rubber-stoppered bottle and sent to the laboratory for analysis. During this process of reduction the sample has unavoidably become partially air dried, but accuracy in calculation to its condition ‘ as received ’ is insured by using for this purpose the 2-oz. portion referred to above.”

The foregoing instructions obviously only apply to the sampling of consignments of fuel ; the sampling of coal in the mine is dealt with in the report mentioned, but this is a matter requiring great experience, and one in which the mining engineer’s opinion is invaluable.

Treatment of Laboratory Samples.—The fuel analyst often receives a sample of coal of several pounds weight, which must be greatly reduced both in bulk and in size of individual particles before it can be analysed.

The best method of procedure is to weigh the sample as received, and then to expose it in a large iron tray to the air, until the weight is practically constant. The loss in weight is noted, and the "air-dried" coal is then broken into pieces until all pass through a ½-inch sieve; the whole is well mixed, flattened down, and "quartered"—that is, divided into four sectors—two opposite portions are removed, the remaining two are broken down until they will pass through a ¼-inch sieve, mixed, and again quartered. This operation is repeated until about 2 lbs. of the sample remains. This is *coarsely ground* in an ordinary good grinding mill, and placed in an air-tight tin, after a portion has been removed for subsequent finer grinding. A determination of the moisture *only* is made on this portion. The removed portion is ground until it will *all* pass through a 60-inch mesh sieve, and is then transferred to an air-tight bottle. The general analysis and calorimetric work is done on this sample, and the results are calculated back to the coarsely ground sample, and subsequently to the coal as received. Time does not always allow the air-drying. If it is omitted, the coarsely ground sample must be prepared *very quickly*.

II. ANALYTICAL EXAMINATION OF COAL.

The analytical examination of coal may be either ultimate—that is, a determination of the elements carbon, hydrogen, nitrogen, sulphur, etc., present in the coal—or proximate. The latter is undertaken for commercial purposes more often than the former, and we propose to consider it first.

(*a*) The Proximate Analysis of Coal.

Coal, as usually known, whatever its state of division, contains a proportion of water in addition to the solid constituents, which are usually considered as more characteristic of it. The water may be partly derived from the process of washing which coal undergoes, but in all cases there is a certain amount of water natural to it, which amount will depend on the kind of coal, and also on the atmospheric conditions under which it has been stored. When coal is exposed to a dry atmosphere it will lose water until it is in equilibrium with the aqueous vapour in the atmosphere and there is no further tendency towards loss. If the same coal is exposed to a moist atmosphere it will absorb, or rather adsorb on its surfaces, water from the air until again equilibrium is established. Sea-borne coal will usually contain, when taken from the hold, at least its full charge of water corresponding to saturated air at the temperature of the hold. A determination of moisture must, therefore, always form part of a proximate analysis, and be preliminary to an ultimate analysis of coal.

When the dry coal has been obtained the question arises, How shall a proximate analysis be made? What is usually known as a proximate analysis of coal is in reality nothing of the sort. It is a statement of the manner in which the sample will behave when subjected to a rigidly defined heat treatment, which to some extent resembles the operations of gas making or coking in a coke oven. The information furnished by the method is very useful if carefully considered in the light of experience. We describe in this section a greatly improved method of carrying out the coking test which has been introduced by Dr. R. Lessing.

The true proximate analysis of coal by the separation of actual constituents has received but little attention from workers, partly on account of its difficulty, and also because the meaning of results when obtained is not very obvious. We may now consider the various determinations, and the best way of making them.

The Determination of Water in Coal is a matter of great practical importance, since water not only dilutes the coal by taking the place of combustible matter, but also by reason of its high latent heat its effect on the net calorific power of the coal is important. Further, errors in the determination of water affect the results of the determination of volatile matter—*i.e.*, organic matter driven off when the coal is ignited in the absence of oxygen. The subject was investigated in 1899 by a Committee of the American Chemical Society on Coal Analysis,* who recommended the following methods:—

One gramme of the coal is dried in an open porcelain crucible for an hour at 104° to 107° C., preferably in a double-walled bath containing pure toluene. The residue is cooled in a desiccator and weighed in the covered crucible. When the coal contains a high percentage of moisture, it is necessary to make determinations with both the coarse and finely powdered samples. As more moisture will usually be found in the former than in the latter, a correction must be applied to all the other determinations. The amount of this is found by dividing the difference

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* *Journ. Am. Chem. Soc.*, vol. xxi., pp. 1116-1132, 1899.

in the moistures by the percentage of all the other constituents as found in the powdered coal, multiplying the quotient by the percentage of the given constituent, and subtracting the product from that percentage.

Thus, if the moisture in the coarsely-ground sample were found to be 12·07 per cent., as against 10·39 per cent. in the powdered sample, and the volatile combustible matter in the latter 34·25 per cent., the correction factor would be $\frac{12{\cdot}07 - 10{\cdot}39}{100 - 10{\cdot}39} = \frac{1{\cdot}68}{89{\cdot}61}$ $= 0{\cdot}0187$, and the true percentage of volatile combustible matter $34{\cdot}25 - (34{\cdot}25 \times 0{\cdot}0187) = 33{\cdot}61$.

Drying "in Vacuo."—Whilst more water can be obtained by drying the coal *in vacuo* over sulphuric acid than by the above method, the committee consider that the difference between the two (0·37 per cent.) is insufficient to justify the general adoption of the new method in commercial work so long as the conditions of sampling are not more carefully controlled than at present.

It has also been the subject of a report to the Eighth International Congress of Applied Chemistry (1912), by a "Sub-Committee of the Commission Internationale d'Analyses on the Standardisation of Methods of determining Water in Coal and other Fuels, and in Minerals."*

The following is a list of active members of the Sub-Committee:—George T. Holloway (President), J. H. Coste (Vice-President), E. R. Andrews, C. O. Bannister, Prof. Chas. Baskerville, Dr. H. Baucke, W. T. Burgess, Dr. F. Clowes, J. Cohade, Dr. E. J. Constam, Prof. T. Fresenius, Dr. W. F. Hillebrand, H. F. Hills, Prof. W. R. E. Hodgkinson, G. N. Huntly, Prof. M. Huybrechts, A. M'Arthur Johnston, Prof. L. L. de Koninck, G. Lacombe, Dr. R. Lessing, Capt. P. Nicolardot, Dr. W. Pollard, W. E. F. Powney, Dr. W. Rosenhain, C. A. Seyler, Edgar Stansfield, and Dr. J. E. Stead.

ABSTRACT OF REPORT.

This report was written by the president and vice-president, who consulted such members of the sub-committee as were available. It was obviously impossible for the whole sub-committee to meet, but in framing the report every endeavour was made to give due weight to the suggestions and work of those members who communicated with the reporters.

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* Published in *Comptes Rendu* of Commission, in Proceedings of Congress, and in the *Colliery Guardian*, Feb. and March, 1913.

It was not found possible to cover the whole ground of the reference to the committee, but much work was done on one most important branch of the subject, the determination of water in coal, and many useful suggestions on other matters have been received.

THE DETERMINATION OF WATER IN COAL.

On the suggestion of several members of the sub-committee, a series of six samples of coal was sent to members who were able to do experimental work for this report, prepared as follows :—

A quantity of the coal was ground in a Krupp ball-mill and sifted through the 100-mesh standard I.M.M. sieve having $\frac{1}{200}$-inch apertures, and was then exposed for some days in shallow trays so as to be thoroughly air-dried. Lots of about 200 grammes of each sample were tinned off, 30 tins of each sample being charged and sealed at the same time. At uniform intervals during such charging small glass tube samples were taken and immediately sealed with the blowpipe. Some of these have been kept as reference samples ; the remainder have been tested as described in section 5 of this part of the report.

The lever-top tins had been previously tested, and found to be practically, but not absolutely, air-tight. The lids, after being forced into place, were, therefore, sealed by means of rubber solution, which has been proved harmless and effective, and safer and better than soldering. The samples sent out to each member of the committee may be relied upon as being identical, and as truly representative of the air-dried coals.

Table VII. shows the approximate amounts of moisture, volatile matter, and ash in the samples.

TABLE VII.—MOISTURE, VOLATILE MATTER, AND ASH IN COAL.

	SAMPLE NUMBER.					
	1	2	3	4	5	6
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Moisture,	3	10	8	6	7	8
Total volatile matter (*ex* water),	5	35	34	23 (*ex* sulphur)	33	27
Ash,	8	3½	4½	37	8½	10

No. 1 is an anthracite from South Wales.

No. 2 is from the "10-yard" or "thick coal" seam of South Staffordshire (England), which, in many respects, resembles a lignite, and which extends under the whole of South Staffordshire. It has never yet been coked in practice. As mined, it contained 10 or 11 per cent. of water, 5 per cent. of hydrogen, and 13 per cent. of oxygen.

No. 3 is from the Kilburn seam of Leicestershire (England), and is a coking coal largely used for general and household purposes.

No. 4 is a coal from South America, and is interesting in connection with moisture determination, on account of its high sulphur content (4·2 per cent. volatile and 8·2 per cent. non-volatile). No pyrites is visible or can be washed out, but the coal rapidly weathers and develops free H_2SO_4 and $FeSO_4$. It contains 35 per cent. C and 3 per cent. H, and has a calorific value of about 7,000 B.Th.U. Its ash contains about 47 per cent. Fe_2O_3, 17 per cent. Al_2O_3, 35 per cent. SiO_2, only 0·72 per cent. S, and less than 0·5 per cent. of CaO or MgO. As might be expected, it clinkers badly, but it is used locally owing to high cost of imported coal.

No. 5 is an ordinary bituminous coal from Leicestershire.

No. 6 is a somewhat less bituminous coal from the South-east of Scotland.

1. It was found that results obtained by the American "Standard" method of drying for one hour at a temperature of from 104° to 107° C. were only to be relied on when care was taken that the temperature of the coal was definitely as high as is prescribed. The use of air baths, of which the walls and shelves are of varying temperatures, is to be deprecated, since the fact that a thermometer, placed near the vessels containing coal to be dried, indicates the desired temperature is no guarantee that the vessels are at that temperature. It was also found that platinum or porcelain crucibles, especially the former, were less suitable as drying vessels than either well-fitting pairs of watch glasses or well-stoppered weighing-bottles. The variations in the results of various workers, amounting in some cases to 1·5 per cent. of water, were probably due more to the above causes of error than to variation in the water content of the samples.

Drying at 104° to 107° for two hours gave results which, on the average, were lower than those obtained with the same coals dried for one hour. In some cases individual results were higher than those obtained by heating for the shorter period, but the evidence was in favour of the view that any extra loss of moisture which may occur, is more than balanced by the gain in weight due to oxidation. The reporters emphatically state that *no advantage appears to be obtained by heating coal for a longer period than one hour at a temperature of* 104° *to* 107° *for the determination of moisture.*

2. *The methods ordinarily used by different workers* varied considerably. The quantity used was in most cases 1 gramme, but in one case as much as 500 grammes, and in others 25 to 30 grammes and 4 to 5 grammes were taken. The temperatures, or reputed temperatures, varied from 94·5° in the case of a worker at Germiston, Transvaal, which is about 4,000 feet above sea level, to that obtained in a toluene bath, which appears usually to be considered as from 105° to 107°, although toluene boils at 110·7°.

It does not appear that any member of the committee usually employs a vacuum method, although some speak highly of this method.

It must be borne in mind that, in some cases, the adoption of a method does not necessarily indicate that such method is specially favoured by the worker, as it may be prescribed in connection with a specification not framed by him.

There appears to be a preponderance of practice in favour of some modification of the Standard American Method of drying 1 gramme at 105° or thereabouts for one hour, but a majority of workers using this method introduce the precaution of using a vessel—either watch-glasses, weighing-bottle, or boat in tube—which can be closed while it is being weighed.

The results reported are particularly interesting as representing the figure which members would have returned had the samples been sent to them in the ordinary way of practice.

For every coal the maximum is obtained by the worker using a temperature of 105° or thereabouts, although, with the anthracite, two workers who used water ovens were within ·05 of the maximum. It is worth noticing that, although this comparison in no way represents the relative or absolute accuracy of the results, in only one case was the discrepancy greater than 1 per cent., and that the greatest variations calculated on the mean *dry matter* were as follows :—

1	2	3	4	5	6
0·3 %	0·9 %	1·2 %	0·9 %	0·8 %	0·9 %

These errors are probably in all cases less than the errors incident to sampling from a large bulk.

It is realised by the reporters that the occurrence of such large variations between workers, whose methods are relatively free from experimental error, in so far as they each give concordant results, indicates (1) the need for some more definite agreement as to the processes to be used, and (2) further work on the general question of the presence of water in coal and other materials, and its determination.

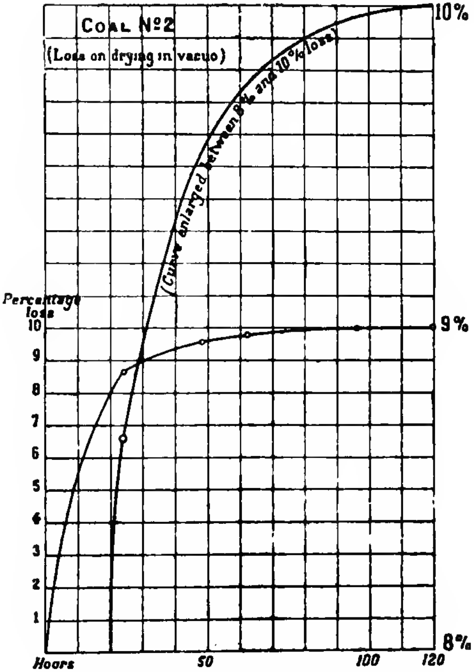

Fig. 22.—Curve showing rate of drying.

3. The results obtained by *the method of drying in the presence of a desiccant under greatly reduced pressure,* vary to such an extent as to militate greatly against the value of the method as one of ordinary application. Although, on *a priori* grounds, the method appears to be almost ideal, many points require attention in

order that the results obtained by different workers may be comparable. The rate of drying by this method will, if (as is most probably the case) the water is adsorbed—retained by surface concentration—follow an exponential curve, the slope of which will depend on the rapidity of the exchange, through the medium of the vacuous space, between the substance to be dried and the desiccant (see Fig. 22). If the temperature be kept constant, this rate will vary with the relative areas of substance and desiccant which are exposed, with the partial pressure of gases other than water vapour, with the absorptive power of the desiccant, with the volume and form of the vacuous vessel used, and the form of the vessel in which the substance to be dried is exposed. In any case, the drying, relatively rapid at first, will soon fall off to a nearly uniform rate, which may continue for days, and the increments of loss of weight may be so small as to appear negligible, whereas their sum over the whole period of drying would perhaps be appreciable. *It is in fact difficult to know when to stop.*

The results actually obtained by workers bear out this conclusion. In a method, such as this, which is practically free from manipulative errors, it is difficult to explain the great variations obtained by different workers otherwise than by supposing that stagnation of vapour, difference of temperature, small exposure of substance to be dried or of desiccant account for the lowness of some of the results. It may be supposed that in all these cases much longer exposure would have caused a greater loss, although there is the chance that, even with a fairly good vacuum, some compensating gain by oxidation may take place, thus invalidating any results obtained in a badly designed desiccator or with a weak desiccant. If the lowness of the vacuum is a cause of slow drying, this possibility becomes still greater.

4. The following methods of determining water, other than those indicated in the president's circular letter, or included in the preceding sections, were experimented with by different workers:—

(*a*) Drying in a water oven.
(*b*) Drying in a current of inert gas.
— Indirect determinations—loss of weight of coal.
+ Direct determinations—gain of weight of drying tube.
(*c*) Drying for ¼ hour at 105° of varying weights of coal spread over varying surfaces.

(*d*) Drying at 105° for varying times (¼ hour to 2 hours).
(*e*) Drying in desiccators at ordinary pressure.
(*f*) Expulsion of water by boiling coal with xylene and measuring the volume of water evolved.

(*a*) The uncertainty (in some cases as much as 16°) as to the temperature in a large water oven, although, judging from an observed small difference between the loss in one hour at 79° and a reputed temperature of 100°—viz., 0·21 per cent.—its effect is not great, renders the use of this appliance undesirable for exact moisture determinations, and we cannot recommend it. *The mere fact that the range of temperature between, say* 80° *and* 98°, *appears to be a particularly insensitive one, and, therefore, allows very concordant results to be obtained under varying conditions, induces a false sense of security, which a few experiments at* 105° *will completely shatter.*

(*b*) The method of drying at 104° to 107° in a current of gas free from oxygen appears to possess a considerable advantage over any other process of drying at an elevated temperature, in that the necessary compromise between the desire to dry completely, on the one hand, and the fear of oxidation on the other, is reduced to a minimum. It may be said, at anyrate when "fixed" gases such as hydrogen, nitrogen, or carbon dioxide are used, that the only reasonable possibility of error is the loss of something other than water, due to the elevated temperature adopted. That this is small, at least for some coals, has been shown by Mahler.* The use of coal gas, unless carefully purified, would seem to be very risky. It is perhaps not unreasonable to suppose that dry coal may possess a certain power of ad- or ab-sorbing some of the constituents of coal gas.

TABLE VIII.—PERCENTAGE OF WATER IN DRIED COAL.

COAL NUMBER.											
1		2		3		4		5		6	
−	+	−	+	−	+	−	+	−	+	−	+
3·15	3·25	10·31	10·68	7·78	8·18	6·09	6·34	7·54	8·01	7·84	8·28
3·19	3·23	10·22	10·38	7·52	8·29	6·42	6·56	7·47	8·37	7·92	8·25

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* *Comptes Rendus*, 1910, p. 1521 (2).

It is worthy of note that, in four coals out of the six sent out, the highest result obtained was by this method.

Two series (Table VIII.) in which the coals were dried at 105° in a current of dry air, and the loss of weight compared with the gain of a drying tube, were intended to show the differences between the direct (+) and indirect (−) methods when the influence of oxygen is not excluded.

5. (1) The actual percentage of water in the samples, and
   (2) Treatment of samples of coal when received.

(1) The question as to the actual percentage of water in the samples sent out by the president and received by workers is important. The method of preparation of these samples appears to have been approved generally by workers.

The results obtained on the reserved tube samples are discussed with a view to obtaining a working convention as to the probable moisture content of the coal in the tins sent out.

In no case was the highest percentage of water found in the tubes as high as the highest found by individual workers in the tinned samples. The reporters feel, therefore, that the tubes are not, on the whole, as reliable as the tins, although the method of sealing the tube prevented any danger of loss of moisture during sealing. It is probable that the operation of sealing, however carefully conducted, may cause some loss of water by convection currents. It is certainly remarkable that, in every case, some tins gave higher results than the tubes.

The reporters have considered the maximum results of individual workers, because it appears to us that the probability of obtaining too high results is, by all the methods described, extremely small, whilst the methods of drying in air, water, or other baths without proper circulation of hot air, and the vacuum methods, are likely to give low results, even with ordinary careful work.

The table of maximum results obtained on each coal by individual workers is interesting, although it is hard to conclude whether it should be taken as illustrating the difficulties of the sampler or those of the analyst.

(2) An important point to consider, in connection with discrepancies between the results of different workers, is the effect of exposure to the atmosphere on the moisture content of coals. The result of the examination of the sealed samples point to the probability that, even when the greatest care is exercised, and

TABLE IX.—SHOWING THE MAXIMUM FIGURE OBTAINED BY EACH WORKER ON EACH COAL AND THE METHODS USED.

Worker.	1	2	3	4	5	6
I. Method,	(2)	(2)	(2, 3)	(2)	(2)	(2)
Result,	2·90	9·70	7·10	5·30	7·10	7·20
II. Method,	(2)	(1A)	(1A)	(1A)	(1A)	(1A)
Result,	3·15	10·25	8·00	6·05	7·68	8·16
III. Method,	(1A)	(3)	(3)	(1B)	(1A, B)	(1A)
Result,	2·92	9·89	7·00	5·91	7·21	7·48
IV. Method,	(4*b*, *di*)	(4*b*, *di*)	(3)	(1A)	(3)	(3)
Result,	3·15	10·46	7·76	6·08	7·60	7·80
V. Method,	(3)	(4*b*, *i*)	(4*b*, *i*)	(4*b*, *i*)	(3)	(3)
Result,	2·85	10·18	7·73	6·24	7·51	7·68
VI. Method,	(2=1A)	(1A)	(1A)	(1A)	(1A)	(2=1A)
Result,	3·15	9·59	7·47	5·38	7·38	7·58
VII. Method,	(3)	(3)	(3)	(3)	(3)	(3)
Result,	3·70	10·39	7·86	6·10	7·72	8·41
VIII. Method,	(1A)	(1A)	(1A)	(4*b*, *i*)	(1A)	(1A)
Result,	3·24	9·92	7·46	6·26	7·32	7·53
IX. Method,	(3)	(3)	(3)	(3)	(3)	(3)
Result,	2·92	9·96	7·52	5·42	7·26	7·56
X. Method,	(1A)	(3)	(3)	(3)	(3)	(3)
Result,	3·16	10·33	7·98	6·22	7·79	8·08
XI. Method,	(3)	(3)	(3)	(3)	(3)	(3)
Result,	3·09	10·31	7·74	6·13	7·66	7·82
XII. Method,	(1A)	(4*b*, *i*)	(4*b*, *i*)	(4*b*, *di*)	(4*d*, *di*)	(4*b*, *i*)
Result,	3·19	10·44	8·03	6·62	7·87	8·12
XIII. Method,	(1A)	(1A)	(1A, B)	(1B)	(1A)	(1B)
Result,	2·96	10·16	7·30	5·90	7·20	7·38
XIV. Method,	(2=4C)	(4D)	(4D)	(4)	(4)	(2=4C)
Result,	3·10	10·16	7·76	6·26	7·60	7·87
XV. Method,	(4*b*, *di*)	(4*b*, *i*)	(4*b*, *di*)	(4*b*, *di*)	(4*b*, *di*)	(4*b*, *di*)
Result,	3·03	10·61	8·18	6·41	7·98	7·94
XVI. Method,	(2)	(3)	(3)	(2)	(3)	(3)
Result,	2·90	9·63	7·20	5·27	7·00	7·11

NOTE.—4*b* : *i* = indirect ; *di* = direct.
The numbers refer to the methods as numbered in the text.

the coal is allowed some days to attain a state of equilibrium with the atmosphere, variations in the water content may occur during the short period necessary for putting up several sets of samples. These differences were probably greater than would occur in ordinary practice, owing to the fact that the coals were very finely ground.

The reporters think that the safest plan of dealing with finely ground samples of coal, under conditions of humidity differing widely from those prevailing at the time of sampling, would be (1) to weigh a large quantity into a shallow dish or, better, a metal tray, and to allow, say, 24 hours for it to reach a state of equilibrium with the atmosphere (longer may be necessary), and then to weigh again and to use this sample, the weight relation of which to the original is known for the determination of water, etc. It should be kept in a tightly-stoppered bottle. Or (2) a series of closely-stoppered weighing bottles, already weighed and preferably very small, might have a measured quantity of coal, known to weigh approximately 1 gramme, shot into each from a little scoop or spoon of suitable size. They could then all be weighed and afterwards put into a large air-tight vessel—say a desiccator vessel—which is filled with CO_2. When a determination is to be made, a bottle can be taken out, and the whole of its contents, as far as may be, tipped into the weighed vessel to be used for drying or other determination, and the bottle re-weighed. By this means a weight slightly less than that originally in the bottle is taken, and the error of assuming that the weight—probably a few milligrammes—left behind represents the coal in its original state is inappreciable. Hence, however long a period after the bottling-off may elapse before a small sample is used, any change of weight is negligible so long as it is not so great as obviously to affect the whole character of the coal.

Another plan which, it is thought, on the whole, when sufficient work has been done, to be most convenient for determination of water in a bulk, is to weigh 50 grammes or 100 grammes, and to determine the water by the xylene method.

It is not advised that ground samples of coal should be emptied from the containing vessel and spread out unless a portion is set apart each time for a determination of water *before* mixing the sample. It is safer to place the sample in a cool place for some time, and then to stir it with a spatula before taking out a portion for the determination of water.

6. A discussion of appliances follows: the nature of the conclusions being sufficiently indicated in the following summary and recommendations:—

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS.

It is not easy to assess, on any very philosophical basis, the merits of the various methods used, but the following considerations have guided us in arriving at conclusions and setting forth recommendations:—

I. There is evidence that no appreciable amounts of hydrocarbons are lost by coal when it is exposed to temperatures not above, say, 140° C. for a time much longer than that required for drying it, although there is evidence that traces of gases are lost under certain circumstances (Dr. Prager has evidence of this, and is working on the subject). Others have noticed that samples of coal which had been sealed appeared to be under some increased pressure when opened.

II. Since the loss of weight when coal is heated to the temperature mentioned above is not appreciably affected by the evolution of hydrocarbon from the coal, the only serious source of error in properly conducted experiments at that temperature is oxidation of coal, which causes an increase of weight as drying is prolonged. The highest results may, therefore, be taken as the most correct. A consideration of the Tables IX. and X. will show at a glance which methods have been found to give the highest results with the various coals.

The question of the detection of added water in coal, which has been raised, presents some difficulty, especially in view of the fact that coal is washed in preparation for the market. It might, at first sight, appear that air-drying would show whether coal contained an excess of water above its normal amount or not. A consideration of the manner in which the water adsorbed by coal will vary with the tension of aqueous vapour of the surrounding air will show that the only way of determining added water would be to find out the percentage of water proper to the coal at the temperature and pressure and tension of aqueous vapour which prevailed at the time of loading, and to compare this with the actual percentage of water. It is only within certain very wide limits that such a determination would be possible.

The conclusions and recommendations which form the next

TABLE X.—WATER IN COAL. AVERAGE PERCENTAGES OF WATER FOUND BY DIFFERENT METHODS.

Method,	1	2	3	4	5	6
1*a*,	2·96	9·84	7·33	5·84	7·20	7·48
1*b*,	2·87	9·64	7·08	5·75	6·98	7·20
2,	2·99	9·76	7·33	5·71	7·23	7·47
3,	2·95	9·97	7·40	5·35	7·27	7·60
4*a*,	2·89	9·65	7·14	5·34	6·96	7·25
4*b* Loss,	2·84	10·12	7·57	6·04	7·29	7·69
4*b* Gain,	2·91	M 10·40	M 7·97	M 6·46	M 7·92	M 7·85
4*c*,	M 3·01	10·03	7·61	6·10	7·55	7·81
4*f*,	3·00	10·38	7·80	6·16	7·74	7·60

M = Highest of the average figures for each coal.

and the final section of this part of the report are presented as reasonable deductions from the facts presented in the body of this report.

The work of the sub-committee may be summarised as follows:—

1. It does not appear that at present there is any means of distinguishing by analysis between "added water," "moisture" (which term we presume signifies water of adsorption—*i.e.*, that due to a concentration of water on the surface of the particles)—and "water of crystallisation" or of "combination," whatever the latter somewhat indefinite term may be supposed to mean.

2. It is probable that the distinction between moisture and water of combination is of little moment in the case of coal, since the losses of water (*a*) at ordinary temperature under greatly reduced pressure, and in the presence of suitable means for reducing the tension of aqueous vapour to an inappreciable quantity (desiccants), and (*b*) at temperatures a few degrees above the boiling point of water, do not differ seriously.

3. Coal is a substance which very readily undergoes oxidation, and the best results in the determination of water can only be obtained when the coal is treated in an atmosphere containing no oxygen.

4. Coal is a very hygroscopic substance and, before being dried, must be properly protected in the laboratory from the effects of changes of temperature or of atmospheric conditions. When dry, it must be protected from any contact with moist air or with moisture in any form until the determination is finished.

5. Unless the initial rate of drying is known to be very rapid, the drying should be divided into two periods, of which the latter is much longer than the former. Unless this is done, it is probable that an almost constant though small increment of loss, continued over a very long period, may be mistaken for an inappreciable total loss.

6. When the initial rate of drying is very rapid—*e.g.*, at 105° or thereabouts—the gain of weight by oxidation may *very soon* become greater than any loss due to a very slow rate of drying over a long period.

7. There is no advantage to be obtained by drying coal at temperatures above that of the atmosphere, but below, say, 105° C.

Those who have read the full report, or who have carefully read the above conclusions, will not need to be informed that the accurate determination of water in a small sample of coal is a matter of difficulty, and requires grave consideration. In the case of large samples of relatively coarse coal, the matter is of even greater difficulty. We put forward the following recommendations, believing them to be sound, and having due regard to the requirements of both the industrial and the research chemist. We do not suggest that they are final, but ask that workers shall give them serious consideration with a view to their general adoption. We recommend that

1. Whenever possible, especially in the case of very moist coals, the water in the original sample should be determined after it has been subjected to a minimum amount of preliminary treatment (*e.g.*, thorough mixing with rapid crushing of lumps) by either of the following methods :—

(*a*) A carefully weighed portion of from 100 to 500 grammes of coal is spread out in a metal tray, and exposed for at least 24 hours to the atmosphere of the sampling room. The tray containing the coal is then reweighed, and the percentage change of weight is calculated. The coal is then coarsely ground in a mill, a ball grinder is best, and the water determined in the ground portion by one of the methods given in recommendations 2, 3, or 4. The water in the original sample can then be calculated.

(*b*) The xylene method used by Dr. Constam ; all results to be calculated back to the original coal.

2. *For ordinary technical work*, coal shall be dried in an oven with a good air circulation for a period not exceeding one hour at a temperature not below 104° nor above 111° C. It is advised that two portions of 1 gramme should be weighed between pairs of accurately fitting watch-glasses, or in a shallow weighing bottle, previously heated to the temperature of drying and cooled in a good desiccator, and be dried for periods of half an hour and one hour respectively, the upper glass or the lid of the bottle being removed during the period of drying, at the end of which it should be replaced loosely and the covered vessels placed in the desiccator to cool. At the end of the period of cooling, which should be equal to that allowed for the heated *empty* glasses or bottles, they should be reweighed and the percentage loss calculated. The higher result should be considered as the percentage of water in the coal. The required temperature can be obtained by the vapour of boiling toluene (110·7° C. at 760 mm.), by steam at a pressure of 906 to 1,100 mm., or by an electrically heated thermostatic arrangement. We advise that a long oven with a door in the small end should be used. A toluene oven with a pre-

heating arrangement for the air current, as described by Siau,* or other similar device, is, in our opinion, a practical arrangement. We strongly condemn air ovens and all devices in which the temperature of the walls of the drying chamber is variable. We believe that a fairly uniform temperature in the whole of the interior of an oven is only to be obtained when the heated walls have an area very large relatively to the cubical contents of the interior, and are themselves at a uniform temperature. A preheated supply of air is preferable. Mere heating without a proper air current is unreliable. Good results can be obtained with larger quantities than 1 gramme, provided not more than 0·3 gramme is taken for each square centimetre of surface exposed.

3. Whenever it is suspected that a coal is specially liable to oxidation or the half-hour and one-hour results differ materially, drying at 104° to 111° in a current of nitrogen or carbon dioxide is to be preferred to drying in an oven through which a current of air is passing. Either the direct or indirect method of estimating water may be used. If the former is chosen, care must be taken to prove the dryness of the stream of gas which is passed over the coal. The percentage of free oxygen in this gas must be inappreciable. This method of drying in a current of inert gas is best for all very exact work.

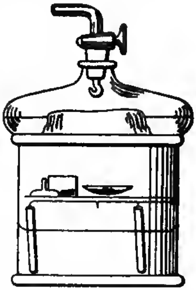
Fig. 23.—Hempel's desiccator.

4. Drying to constant or minimum weight in a vacuum in the presence of sulphuric acid (or other desiccant) possesses no advantage over the last-mentioned method. It is very much slower, and, unless the vacuum is very high, it is better to fill the desiccator with carbon dioxide (or other inert gas) before exhausting. If this method is preferred a Hempel desiccator (Fig. 23), or any other form in which a large surface of sulphuric acid is exposed both above and below the coal, should be used; the coal should be weighed in watch-glasses or shallow weighing bottles, and the loss after, say, 24 hours, 72 hours, and 144 hours should be taken.

With such prolonged periods of drying, the results obtained by this method are practically identical with those by method 3. The air admitted into the vacuous space should always be dried by passing it slowly through or over sulphuric acid.

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* *Journ. Soc. Chem. Ind.*, 1911, p. 61.

5. The method of driving off water from coal by heating it in boiling xylene and measuring the water which distils over with the hydrocarbons, is a variant of the method of drying in an inert atmosphere at an elevated temperature. It is worthy of serious consideration, and although we cannot, in view of the limited information at our disposal, recommend it unconditionally, we consider that it is most promising and appears to be particularly suitable for industrial purposes.

6. Coal should always be weighed in closed vessels with well fitting lids or stoppers. Deep vessels, such as crucibles, are unsuitable for water determinations. Porcelain or metal boats which can be weighed in stoppered or well-fitted sliding tubes may be used.

7. Desiccators with the strongest sulphuric acid, *frequently* renewed, are recommended. If calcium chloride is used, it must be ignited before it is put in the desiccator. If phosphoric anhydride is used, it must frequently be stirred. These substances are not so convenient or reliable as sulphuric acid.

(Signed) George T. Holloway (Pres.).
(,,) J. H. Coste (Vice-President).

The subject of the determination of moisture generally has been treated by G. N. Huntly and one of us recently.*

Appliances for Drying Coal.—We describe two appliances designed by one of us which have in our practice been found useful for drying coal and other materials under the conditions mentioned.

An Air Bath, which has been found useful for drying coal at temperatures above 100° C. in a current of gas. It is made from a square copper box, with a lid perforated at the top to take a thermometer (*T*), the bulb of which is level with the tubes (*A* and *B*) passing through the sides of the box. It is heated by an Argand burner and supported on a retort stand. Dry air (or other gas) passes through the tube *B*, where it undergoes a preliminary heating, and then through the drying tube *A*. The substance to be dried is placed in a porcelain or nickel boat. It is usually sufficient to estimate the loss in weight of the substance in the boat; but drying tubes can be used to collect the water.

When a thermo-junction was placed in coal in a boat inside

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* *Journ. Soc. Chem. Ind.*, vol. xxxii., 1913, pp. 62-67.

the drying tube and another in the same circuit wrapped round the thermometer, it was found that the temperatures only differed by a degree when a water-pump was drawing air through the system at the rate of about 8 litres per hour. If this bath is protected from draught any reasonable temperature can easily be maintained within a few degrees.

An *oven* in which several determinations of water can be made simultaneously, which can be maintained at a known, constant, and uniform temperature, and through the whole of which a sufficient stream of hot air or other gas freely circulates, is frequently desired. The apparatus described fulfils these conditions.*

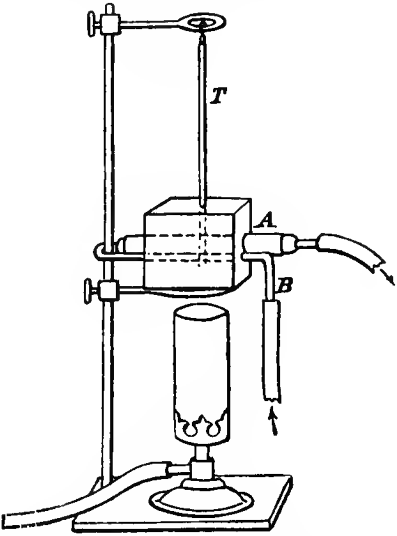

Fig. 24.—Air bath with preheating tube.

A cylindrical copper vessel (*A*, Fig. 25) placed horizontally contains a suitable quantity of a pure liquid, the boiling point of which approximates closely to the desired temperature. It is heated by a series of gas jets and the vapour is condensed at *B* and returned. The muffle-shaped drying chamber *C*, *C* is

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* Coste, *Journ. Soc. Chem. Ind*, vol. xv., p. 417.

surrounded, with the exception of about $\frac{1}{30}$ of its total external surface (the door), by the boiling liquid or its vapour. Air which has passed through a very much flattened tube *D*, *D*, lying under, but not in contact with, the drying chamber, enters it at the bottom of the end which is in the vapour, and leaves through a slit, communicating with a chimney *F* in the door,

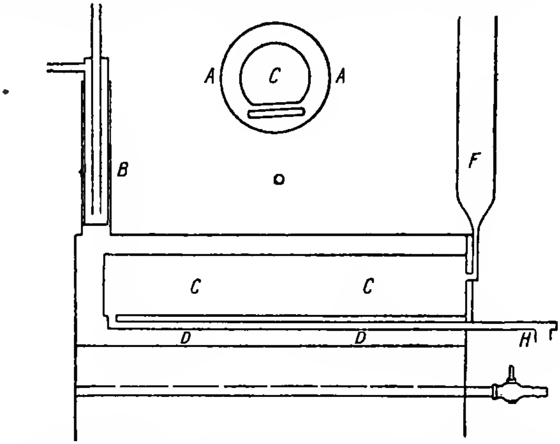

Fig. 25.—Water or toluene drying oven with preheating tube.

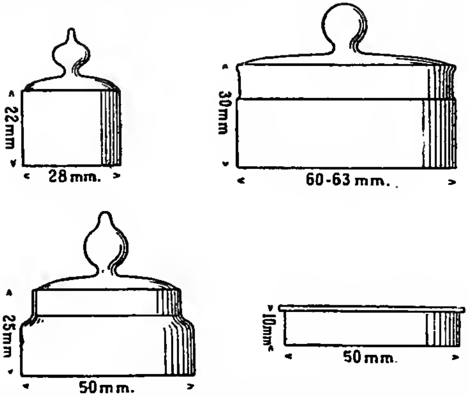

Fig. 26.—Weighing vessels for moisture determination.

which is fixed tightly against the end of the chamber by means of steam rubber jointing, and a screwed hinged bar against the end of the oven. The cubical contents of the drying chamber are very small relatively to the area of heated surface. If desired the air may be dried before it enters the preheater at *H*, or other gases such as carbon dioxide or nitrogen may be used.

The drying chamber will take, on a copper tray which cannot be pushed back so as to close the air inlet, six watch-glasses or flat weighing bottles. Drying goes on equally well in any part of the oven, and substances placed in it quickly attain a temperature within 1° of that of the vapour.*

We show (Fig. 26) various forms of weighing bottles mentioned in the committee's report, and designed to expose a large surface of coal to the action of dry air. As a matter of fact, we find that small "tins," such as vaseline is sold in, serve better than any glass vessel. They are very light, expose a large surface of coal, conduct heat very rapidly, so that coal quickly attains the temperature of the oven, and are sufficiently air tight. It is best to invert the "tin" using the lid as containing vessel and the body of the tin as a cover.

The Determination of Volatile Combustible Matter in Coal (Standard American Method).—One gramme of the fresh undried powdered coal is heated for seven minutes over the full flame of a Bunsen burner, in a platinum crucible weighing 20 to 30 grammes, and provided with a tightly fitting cover. The bottom of the crucible, which is supported on a platinum triangle, should be from 6 to 8 cm. above the top of the burner. The flame when burning free should be 20 cm. high, and care should be taken to protect it from draughts during the determination.

The under surface of the cover should remain coated with carbon, but the upper surface should keep free from it. The most serious objection brought against this method is that the rapid heating causes mechanical loss in the case of certain non-coking coals, but the committee state that no evidence has been given as to the amount of such loss, whilst in certain experimental determinations which are described, they show that the loss can only have been insignificant. They consider that any method chosen as the standard one for this determination should give, as far as possible, results approximating closely to those obtained in the commercial manufacture of coke, and that it should be capable of such accurate description that concordant

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* Coste, *Journ. Soc. Chem. Ind.*, 1912, p. 471

results should be obtained by different workers with the same samples of coal. They give certain results as favourable evidence, as far as they go, as to the method described above fulfilling the first condition, but have no evidence on the second point.

Ash.—The residue left in the determination of the moisture is ignited at first over a low flame with the crucible open and inclined, until free from carbon. Although any pyrites present is converted almost entirely into ferric oxide in the determination, so that the weight of the ash is less than the weight of the mineral matter, by five-eighths of the weight of the sulphur, the committee do not recommend a correction in proximate analyses. Such a correction, however, is necessary in calculating the calorific power of the coal from analytical data.

Determination of Fixed Carbon in Coal.—This is obtained by deducting the percentage of ash from the percentage of coke left in the determination of the volatile combustible matter. Sulphur is not considered in the calculation.

Coking Tests of Coal when performed under standard conditions—which include the use of apparatus of uniform dimensions, size of flame, and heating for a definite period of time—give one an idea of the behaviour of the coal when heated, the nature of the coke thus obtained, and the amount of decomposition which the coal undergoes. The object of the test originally was merely to determine this last point, but valuable information may be obtained as to the nature of the coke resulting from what is really a "coking" test.

Constam and others worked for several years comparing the different methods suggested for making this test, and on comparing the results of the best known methods, not only with each other, but also with those obtained when working on a large scale, they came to the conclusion that the most satisfactory results were those obtained by the above-described "American method," the details of which were published in the *Journal of the American Chemical Society*, vol. xxi., p. 1122.. The report of the Committee on Coal Analysis of the American Chemical Society represents so far the best organised attempt to place the methods of coal testing on a uniform basis, and although issued in 1899, its recommendations are still regarded as sound, and have not been superseded.

Dr. Pollard * gives the following description of the method

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* "Coals of South Wales." *Memoirs of the Geological Survey, England and Wales*, 1908.

employed by him :—One gramme of the coal is heated for seven minutes exactly in a platinum crucible with well-fitting cover, supported on a platinum triangle over a Bunsen burner, giving a flame 20 cm. high. The bottom of the crucible should be 8 cm. above the mouth of the burner ; gas pressure should be 50 mm. of water (2 inches). The particulars of the crucible used are—height 40 mm., diameter at base 24 mm., at top 34 mm. Capsule cover. A cylinder of clay or asbestos board should be used to prevent draughts from influencing the flame during the operation.

The loss in weight after heating *minus* the percentage of water gives the amount of volatile combustible matter.

It will be noticed that Pollard adheres to the recommendations of the Committee of the American Chemical Society, but gives supplementary information as to the dimensions of the crucible used.

Our experience of the method is that concordant results are obtained by different workers using the same coal, but in the cases of some coals which intumesce considerably, the swelling of the coal seems to be limited only by the size of the crucible. This difficulty has been overcome by Lessing, who has designed "A New Apparatus for the Coking Test of Coal" (Fig. 27), the details of which are given in a paper read before the Society of Chemical Industry, May 31, 1912. The quantitative results given agree extremely well with those obtained by the American method, but the character of the resulting coke is seen to much greater advantage.

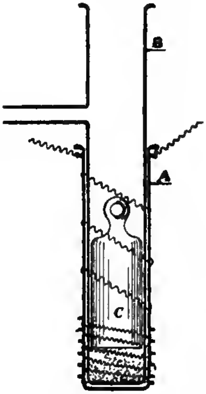


Fig. 27.
Lessing's coking test apparatus (and plates).

The apparatus consists of an outer quartz glass tube (*A*), around which an electric resistance heating coil of platinum wire is wound. The reacting vessel proper (*B*) is a flanged quartz glass tube, which fits loosely into the heating tube, and has an internal diameter of about 10 mm. The coal (1 gramme) is weighed into this tube, and a third tube also made of quartz glass (*C*) fits loosely into the reacting tube, and is placed on top of the coal before the commencement of each test.

By varying the weight of this tube, or by placing different weights of quartz powder in it, the pressure on the coal during the test may be altered.

The heating tube is permanently embedded in an insulating material, such as Kieselgühr. The temperature can be regulated by the adjustment of the current flowing round the tube.

The following photographs (Plates I. to V.) show the advantage of Dr. Lessing's method over the American method, and justify his conclusion that " the practical value of this apparatus seems to me to lie principally in the fact that the coke obtained in it brings out the peculiarities of the coal in a much more striking fashion than does the coke in the crucible test."

Gas-Making Tests.—*The value of a coal for gas-making* may to some extent be predicted by carbonising a representative sample of the coal in the retort of an experimental gas plant, which comprises all the necessary appliances for washing, purifying, and measuring the gas obtained. When all the gas has been driven off, the coke is withdrawn from the retort and transferred to a sheet-iron water-tight box fitted with a lid, the whole being immersed in cold water until the coke is sufficiently cool to weigh. The volume of the gas is noted, as is also the volume of tar and ammoniacal liquor obtained from the condenser and washer.

The weight of coal carbonised is 2·24 lbs., and this being one-thousandth part of a ton, the yield of products per ton is readily ascertained.

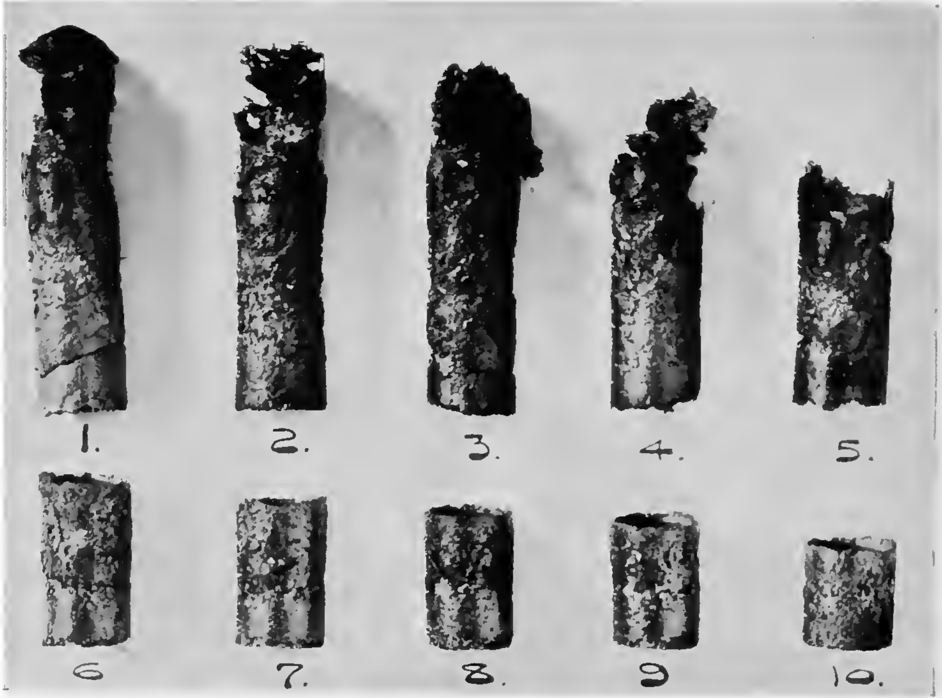
Obviously the results obtained could not be expected to be identical with those obtained on a large scale, but they afford sufficient information to the experienced worker to justify the use of the apparatus, provided that its limitations are recognised (see Coste, *Cal. Power of Gas*, p. 105).

Determination of Ash in Coal.—This is the least satisfactory figure obtained in the proximate analysis of coal (or in any other naturally occurring organic matter), the reason being that what is weighed as non-combustible matter is not necessarily of the same composition as the mineral matter originally present. A commonly occurring mineral in coal is iron pyrites, FeS_2; this compound, when heated in a current of air, is converted into ferric oxide, Fe_2O_3, the sulphur being driven off as sulphur dioxide.

Now, 240 parts by weight of pyrites yield 160 parts by weight of oxide of iron—that is to say, the residual ash weighs only two-thirds of the weight of the original mineral matter, and

PLATE I.

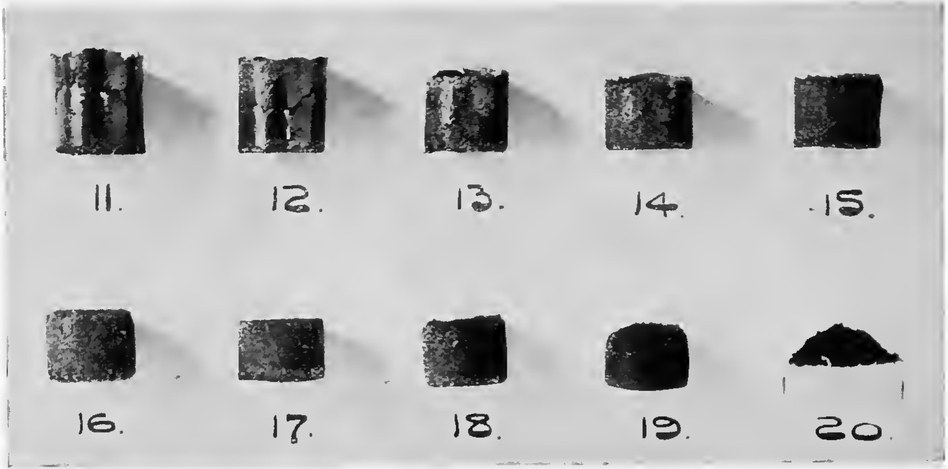
[To face p. 104.



Cokes (1-10) obtained from Different Coals.

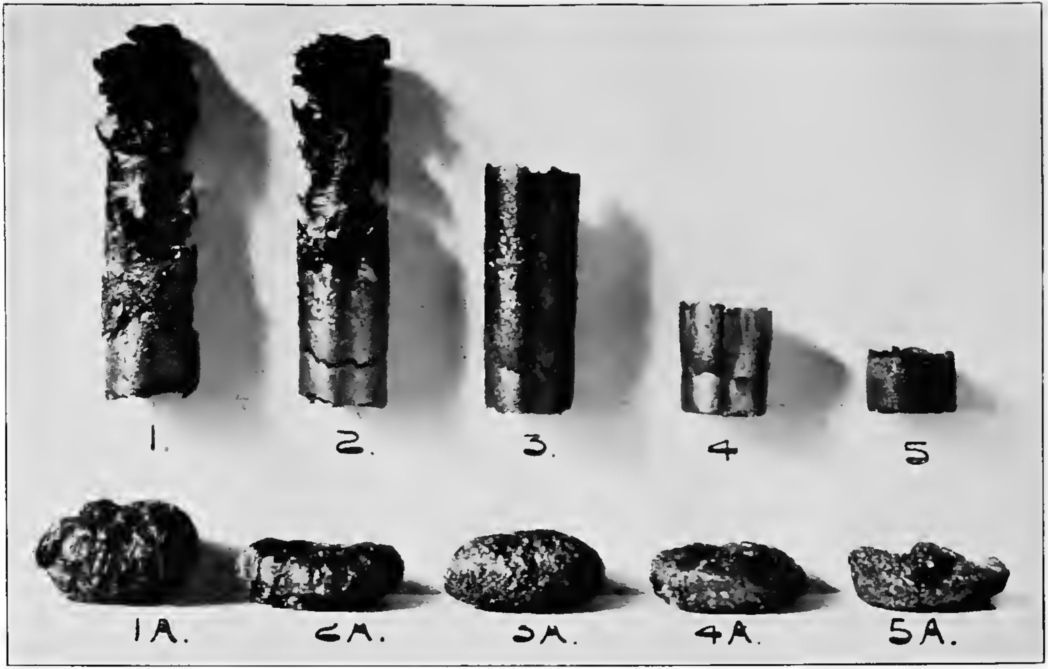
PLATE II.

[*To face p. 10*[illegible].



Cokes (11-20) obtained from Different Coals.

PLATE III. *[To face p. 104.*



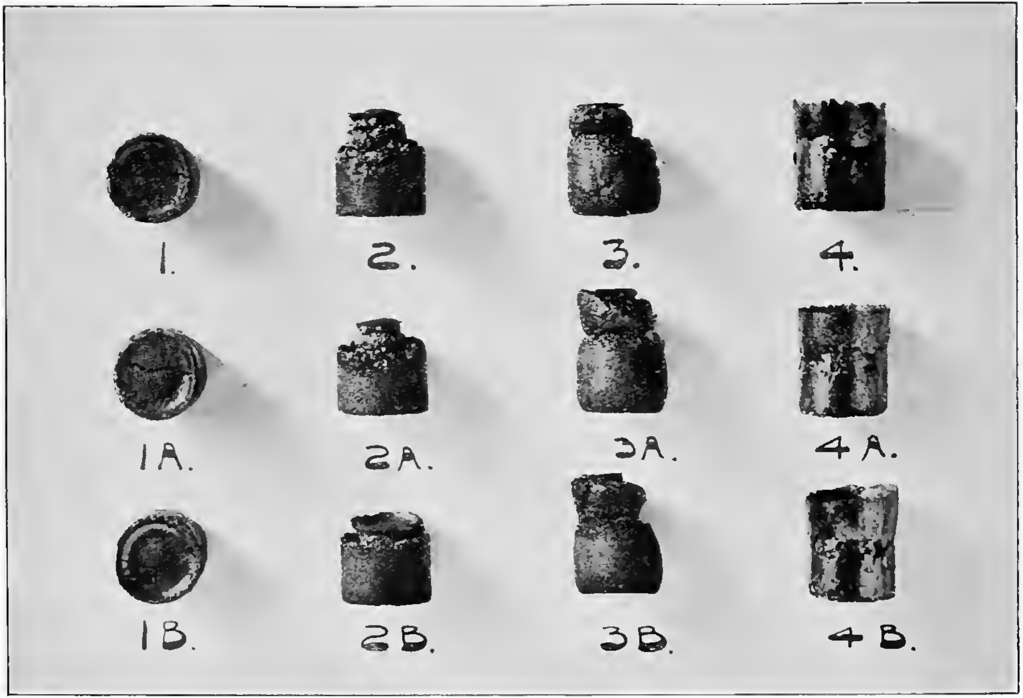
Comparison of Cokes obtained by New Method and by Old Crucible Method.

PLATE IV.

Sections of Coke Specimens from Different Coals.

PLATE V.

[*To face p. 104.*



Showing Constancy of Shape and Character of Coke obtained from each Coal.

consequently when determining the ash of a coal containing 3 per cent. of pyrites the ash is 1 per cent. low on this account only. We shall refer to this particular instance again when dealing with the "ultimate" analysis of coal.

Another possible source of error in the determination of ash is the presence of carbonate of lime. Should the temperature at which the ignition is conducted be too high some, or all, of the carbon dioxide will be driven off, and the resulting ash figure will be correspondingly low. This, however, may be obviated, and we have found that the ignition of 1 gramme of the finely powdered coal in a shallow platinum dish over an ordinary luminous Argand flame is the most satisfactory method of making the determination. In the case of bituminous and ordinary steam coals it is fairly expeditious, the time occupied being about 45 to 60 minutes; with anthracites and cokes it is naturally a more prolonged operation, and we then prefer a muffle furnace, in which the temperature is not allowed to exceed that of a dull red heat.

The sum of the percentages of moisture, volatile combustible matter, and ash subtracted from 100 gives the percentage of "fixed carbon." It will have been noticed that the results obtained in the so-called proximate analysis do not really represent any kind of analysis, but are rather quantitative expressions obtained by working under set conditions.

Extraction of Coal by Solvents has been studied by Prof. P. Phillips Bedson,* who, in a note read before the North of England Institute of Mining Engineers, referred to his work in this direction which had been carried on during the previous eight years. He found that pyridine extracted a considerable proportion of the solid matters of coal, and that bituminous coals yielded greater amounts than anthracites. The dissolved portion when separated from the pyridine was found to be rich in volatile constituents, and to intumesce greatly when submitted to a coking test.

Wahl † extracted a number of finely powdered coals with pyridine. The amount dissolved varied from 18 to 25 per cent., except in the case of anthracites, of which very little was soluble.

The amount of volatile matter in the coals after extraction was usually from 3 to 5·8 per cent. The extracted matter was found to be an amorphous brown powder, the ultimate analysis

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* *Journ. Soc. Chem. Ind.*, vol. xxvii., 1908, p. 147.

† *Comptes Rendus*, 1912, cliv., pp. 1094-7.

of which did not differ greatly from that of the original coal. It was found to contain a slightly greater proportion of hydrogen.

J. C. W. Frazer and E. J. Hoffmann (*Technical Paper* 5, *U.S. Bureau of Mines*, 1912) subjected a finely powdered non-coking bituminous coal to repeated extractions with phenol at about 140° C. They obtained about 10·9 per cent. of soluble matter from the pure "coal substance" (*i.e.*, coal *minus* moisture and ash), the analysis of which indicated that it consisted apparently of almost pure hydrocarbons containing small quantities of oxygenated compounds.

Carbonisation of Coal at carefully regulated Temperatures.—M. J. Burgess and R. V. Wheeler* have done some exceedingly valuable work on the "Volatile Constituent of Coal." Their work may be summarised in their own words, as follows:—

"Presumably, therefore, coal contains two types of compounds of different degrees of ease of decomposition; the one, the more unstable, yielding the paraffin hydrocarbons and no hydrogen; the other, decomposed with greater difficulty, yielding hydrogen alone (or, possibly, hydrogen and the oxides of carbon) as its gaseous decomposition product.

"'Fractional' distillation of coal in a vacuum confirms this view. It is possible by prolonged exhaustion at a low temperature to remove entirely the paraffin-yielding constituents, and leave behind a compound which decomposes at a higher temperature, and yields hydrogen."

(*b*) The Ultimate Analysis of Coal.

This includes the determination of carbon, hydrogen, nitrogen, and sulphur on the previously dried coal. Logically it should also include the determination of the various constituents of the "ash," but this is not usually done. After making the necessary deduction for ash, the difference between 100 and the sum of the percentages of these constituents is taken as representing the percentage of oxygen, which is an unsatisfactory proceeding, but, there being no means of determining oxygen directly, we have no other course to adopt. The importance of the ultimate analysis becomes evident when the question of classifying coal has to be considered; for this purpose it is necessary to know the amounts of carbon and hydrogen contained in the coal free from ash and moisture, and it is possible to determine these two

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* *Trans. Chem. Soc.*, 1910, p. 1917; 1911, p. 649.

elements with considerable accuracy. Another purpose for which the ultimate analysis is sometimes required is for the calculation of the calorific power of a fuel from the results thus obtained.

The value of such a calculation is discussed in Chap. VIII., and we will content ourselves for the moment by remarking that if this were the only reason for conducting an ultimate analysis we should never do it.

Determination of Carbon and Hydrogen is made in the same apparatus as is required for determining the ultimate composition of organic substances. It usually consists of :—

(i.) A purifying and drying system for the removal of carbon dioxide and water from the oxygen and air used during the combustion.

(ii.) A combustion furnace, and a combustion tube of Jena glass or silica, packed so that oxides of sulphur and nitrogen produced during the combustion may be fixed and decomposed respectively.

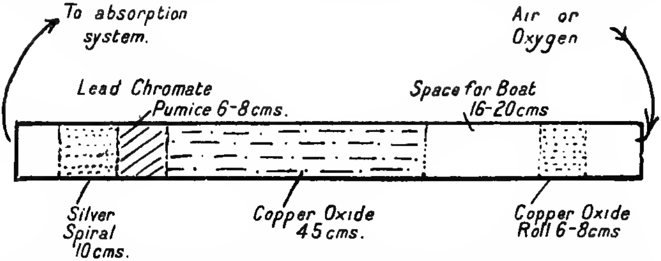

Fig. 28.—Diagram of combustion tube for carbon and hydrogen determinations. Length of tube, 110 cm.; internal diameter, 12 to 15 mm.

(iii.) A weighed system of absorption tubes, whereby the water and carbon dioxide produced may be collected and their weight determined.

The apparatus for purifying and drying the air and oxygen needs no special description, all that is necessary is to be certain that the gas entering the combustion tube is free from moisture and carbon dioxide. This is best ascertained by conducting a blank determination when the whole apparatus is set up, and observing if any increase in weight of the absorption tubes has occurred, or by letting the gas pass through a weighed system of tubes similar to those used for absorbing the products of combustion before it enters the combustion tube.

The following is a description of the tube used by Pollard in his work on the coals of South Wales :—

Length of tube 110 cm., internal diameter 12 to 15 mm.

The diagram (Fig. 28) illustrates the manner of packing the tube.

The apparatus which is used for absorbing the moisture and carbon dioxide produced, consists of tubes containing pumice, which has been specially prepared and then soaked in concentrated sulphuric acid for the former; and similar tubes containing soda lime followed by a desiccant for the latter. There are many different forms of tubes used for this purpose; those designed by Haldane and Pembry* are extremely good. They are used in pairs, and consist of a pair of thin glass test tubes, each tube measuring 4 × 1 inches, and provided with a double-bored cork about ½ inch thick, and fitted with glass tubing, as shown in Fig. 29. The pair (*a*) is for the absorption of moisture. Another pair of tubes (*b*) is used for absorption of carbon dioxide, the first of which is packed with soda lime, the second with sulphuric acid pumice, the object of the latter being to absorb any moisture given off by the soda lime when carbonating. Each pair of tubes when filled weighs about 80 grammes, and for accurate weighing it is recommended that similar pairs of tubes be used as counterpoises. In Fig. 29 the tubes are fitted with ordinary corks which have been previously "paraffin waxed"; they are pushed in flush with the tops of the tubes and a layer of wax finally applied to the top of the corks. To obviate the use of the paraffined corks, pairs of tubes fitted with glass stoppers have been designed by Mr. W. Blount.

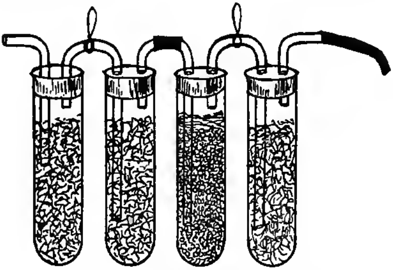

Fig. 29.—Haldane's drying tubes.

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* *Phil. Mag.*, p. 306, 1890

We do not propose to give a detailed description of how to conduct a combustion. It is essentially an operation which requires considerable experience before one can feel confident that the results are correct; moreover, a few discordant results at the commencement are, as a rule, the best incentive to mastering the business. The following are some useful points to be noted:—

The front portion of the long layer of copper oxide should be maintained at a fairly bright red heat, so as to ensure the complete oxidation of any methane, as this gas requires a high temperature for combustion (*cf.* Dunstan and Carr, *Proc. Chem. Soc.*, 1896, pp. 48, 49). The rest of the copper oxide is best maintained at a lower temperature.

The lead chromate pumice, which fixes any oxides of sulphur present, should not be heated above a low red heat, whereas it is essential that the silver pumice should be at a bright red heat, in order that the oxides of nitrogen may be decomposed. It is obvious that acid oxides of sulphur and nitrogen, if not removed in this way, would be absorbed in the sulphuric acid and soda lime tubes, and cause serious errors in the carbon and hydrogen determinations.

The coal to be burned is first dried in a toluene oven, and after cooling for about fifteen minutes in a desiccator the weight of dried coal is ascertained. It is preferable to dry it in a platinum or porcelain boat, preferably the former, so that it may be transferred expeditiously to the combustion tube, which has been heated to the required conditions while the drying has been in progress. Immediately before placing the boat in the tube the weighed absorption tubes should be connected to the tube, and a gentle current of oxygen admitted, the rate of which should be such that the bubbles, as observed in a small sulphuric acid bottle placed between the drying apparatus and the combustion tube, should be "detached," and not appear as a chain of bubbles.

When all is in readiness the boat is introduced and the heating of the hitherto cold end of the tube is started under the roll of copper oxide, *one burner* at the time of introduction, and the next when the tube above the first burner is obviously hot. The boat is then heated, first at the end nearer the inlet of the tube, and heating is so conducted that gas and tar shall come off slowly and be passed forward by the current of oxygen, to be burnt, the former in the red-hot part of the tube, and the latter to some extent when the cooler copper oxide on which it has condensed is heated. By proceeding in this manner the combustion proceeds regularly and quietly, and one is not likely to get what we have sometimes seen — namely, violent deflagration and miniature explosions in the tube.

As soon as the combustion of the coal in the boat is finished—this one can observe by opening the tiles at the portion of the tube where the boat is placed—a current of air is substituted for the oxygen, and the sweeping out of the products of combustion is completed.

The weighed absorption apparatus is removed to the balance case, and if it has not been covered with a cardboard box, wiped, and in any case allowed to stand for about 30 minutes. It is then weighed. The increase in weight of the sulphuric acid tube is due to the water produced, and this weight multiplied by $\frac{1{\cdot}008}{9{\cdot}008}$ gives the amount of hydrogen.

The weight of carbon dioxide is the observed increase in weight of the soda lime tube, and this weight multiplied by $\frac{3}{11}$ gives the weight of carbon.

About 0·5 gramme of coal is usually taken for analysis, and it is advisable to use a freshly packed soda-lime tube for each determination.

Nitrogen is best determined by Kjeldahl's method—heating 1 gramme of the coal with 20 c.c. of concentrated sulphuric acid and about 10 grammes of anhydrous potassium sulphate in a Kjeldahl flask until the liquid is colourless. The contents, when cool, are transferred to a steam distillation apparatus—rendered alkaline by the addition of caustic soda solution, and distilled into a known volume of $\frac{N}{10}$ standard acid. When the distillate measures about 250 c.c., the flask is removed and neutrality restored by addition of a standard alkali ($\frac{N}{10}$); methyl orange is used as indicator.

One c.c. of $\frac{N}{10}$ acid is equivalent to 0·001401 gramme nitrogen. A blank determination should be made on the reagent employed.

Sulphur.—This is best determined by means of the bomb calorimeter, and we shall deal with this method in the chapter dealing with the corrections to be made when determining the calorific power.

An alternative method, recommended by the Committee on Coal Analysis of the American Chemical Society, is as follows:—

One gramme of the finely powdered coal is thoroughly mixed with 1 gramme of light, porous magnesium oxide (*magnesia levis* of the B.P.), and 0·5 gramme of dry sodium carbonate, in a thin platinum dish of 75 to 100 c.c. capacity.

The dish is very cautiously heated by means of an alcohol lamp, not by a gas flame, which may introduce traces of sulphur, whilst the mass is constantly stirred until strong glowing has ceased. The temperature is then gradually increased until in fifteen minutes the bottom of the dish is of a dull red heat. After the carbon has been burned away the mass is transferred to a beaker, and the dish washed with about 50 c.c. of water. The liquid is oxidised by boiling for five minutes with 15 c.c. of saturated bromine water. The insoluble matter is allowed to settle, and, after decantation of the supernatant liquid, boiled a second and third time with 30 c.c. of water. The filtrate, which should be about 200 c.c. in all, is rendered acid with 1·5 c.c. of concentrated hydrochloric acid, boiled to expel the bromine and the sulphuric acid precipitated with 10 c.c. of a 10 per cent. solution of barium chloride added, drop by drop, to the hot liquid. In the case of a coal containing much pyrites or calcium sulphate, the residual magnesium oxide should be dissolved in hydrochloric acid, and the solution tested for sulphuric acid. The sulphur, if any, in the reagents should be determined by making a "blank" with materials only.

"Pure Coal" or "Coal Substance."—The percentages of carbon and hydrogen are returned on what is known (for want of a better term) as the "pure coal" or "coal substance." This is understood to consist of carbon, hydrogen, oxygen, and nitrogen. The sulphur is considered as being present as either sulphates or pyrites, or both. Assuming this to be the case, it is evident that we should determine the sulphur remaining in the ash, and subtract the amount so obtained from the total percentage of sulphur. This would give us what is usually known as the *combustible sulphur*, and this is assumed to have been present originally as pyrites, FeS_2. We must, therefore, increase the amount of ash by $\frac{120}{64} = \frac{15}{8} \times$ (the percentage of combustible sulphur), and decrease it by the equivalent amount of ferric oxide. That is to say, for a coal containing 1 per cent. of combustible sulphur, the ash must be increased by 1·875 per cent. and decreased by 1·25 per cent.—*i.e.*, a net increase of 0·62 per cent., or $\frac{5}{8}$ of the combustible sulphur.

Again, if the mineral matter originally present contains carbonate of lime, it is essential that the amount of carbon dioxide shall be determined in the coal before ignition, or in the ash as determined by the method which we advise, and in the ash remaining in the boat. The difference between the two results will represent the amount which has been driven off in the combustion tube and absorbed in the soda-lime tube. Then we must deduct the amount of CO_2 from the weight of the tube and add the amount on to the ash obtained in the combustion. By so doing, we arrive at the ultimate composition of the coal as accurately as is possible with our present knowledge.

For Example.—We will assume that a coal on examination gave the following figures :—

Dried Coal.

A	Carbon,	85·00
	Hydrogen,	3·00
	Nitrogen,	1·00
	Oxygen,	1·00
(Total)	Sulphur,	2·00
(Combustion tube)	Ash,	8·00
		100·00

Now we want, for the purpose of classification of the coal, to know the carbon and hydrogen when calculated on the "coal substance."

We will suppose that the ash left in the boat contains 1 per cent., and that the dried coal contains 1·5 per cent. of carbon dioxide; further, the ash contains sulphur (in the form of sulphates) to the extent of 0·5 per cent. To obtain our corrected ultimate analysis, we must increase our ash by 0·5 per cent. to allow for the carbon dioxide driven off in the combustion tube.

Again, the " combustible sulphur " equals (2·00 — 0·50) = 1·50 per cent.

$$\frac{1·50 \times 15}{8} = \frac{22·5}{8} = 2·81 \text{ per cent. } FeS_2,$$

which is equivalent to 1·87 per cent. Fe_2O_3.

Therefore we must add 2·81 per cent. and deduct 1·87 per cent., which equals a net addition of 0·94 per cent. to the ash deter-

8·00 per cent.
0·50 ,,
0·94 ,,

mination. Hence our new corrected ash figure = 9·44 ,,

B	Carbon,	84·86
	Hydrogen,	3·00
	Oxygen,	1·70
	Nitrogen,	1·00
	Ash,	9·44
		100·00

The carbon figures will obviously be $\frac{3}{11}$ of 0·5 per cent. too high = 0·14 per cent.; the hydrogen and nitrogen are unaffected; the oxygen figure being taken as difference is naturally seriously altered.

The ratio of carbon to hydrogen in the coal substance in the corrected and uncorrected analyses is as follows:—

	A.	B.
Carbon,	94·44	93·71
Hydrogen,	3·33	3·31
Oxygen,	1·11	1·88
Nitrogen,	1·11	1·10
	99·99	100·00
	C/H ratio 28·4.	C/H = 28·3.

We have had occasion to refer repeatedly to "coal substance" or "pure coal," and have mentioned that it is represented by the sum of the amount of carbon, hydrogen, oxygen, and nitrogen found from the ultimate analysis. We may as well state at once that there is no scientific justification for assuming such to be the case. No doubt a proportion of the mineral matter and moisture may be merely adventitious, but there is no reason why the whole amounts of these substances should be so regarded. Again, the sulphur is considered as being present as either pyrites or sulphates only, but this is hardly probable; it is more than likely that some portion of it exists in combination with the non-mineral portion of the coal.

It is true that the general assumption that "pure coal" consists only of the four elements named enables one to compare results of different workers more readily, and is, in consequence, a valuable working convention, but it should be considered only as such, and not as a rational statement of composition.

III. THE CLASSIFICATION OF COALS ON THE RESULTS OF ANALYSIS.*

The classification of coals has been recommended on various data, which include—

(1) Percentage of carbon and hydrogen, calculated on pure coal.

(2) The relative proportion of carbon to hydrogen—that is, the C/H ratio.

(3) The relative proportion of coke to volatile matter—that is, the fuel ratio.

(4) Volatile carbon $\times \frac{100}{\text{total carbon}}$, with due consideration of "inert volatile."

(5) Fixed carbon with due consideration of total carbon in pure coal.

We may state at once that the data obtained for Nos. (3), (4), and (5) are not of the same order of accuracy as in Nos. (1) and (2), as has been explained when dealing with the subject of "Proximate Analysis," and we do not propose to consider them.

C. A. Seyler's System of Classification is based on the percentage of carbon and hydrogen, calculated on the pure coal. The hydrogen determines the genus and the carbon the species. Pollard considers this classification, although not perfect, is one of the best, if not the best, so far available.

The United States Geological Survey have finally adopted a classification, based on the proportion of carbon to hydrogen, the proposed limits being—

TABLE XI.

		C : H Ratio.
A.	Graphite,	∝ to ?
B.	Anthracite,	? to ? 30
C.		? 30 to ? 26
D.	Semi-anthracite,	? 26 to ? 23
E.	Semi-bituminous,	? 23 to 20
F.	Bituminous,	20 to 17
G.		17 to 14·4
H.		14·4 to 12·5
I.		12·5 to 11·2
J.	Lignite,	11·2 to ? 9·3
K.	Peat,	? 9·3 to ?
L.	Wood (cellulose),†	7·2

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* See W. Pollard, *The Coals of South Wales*; C. A. Seyler, "Chemical Classification of Coal," *Proc. S. Wales Inst. Eng.*, vol. xxi., p. 483; vol. xxii., p. 112. Also "Analysis of British Coals and Coke."

† Wood is not cellulose.

TABLE XII.—SEYLER'S CLASSIFICATION OF COAL.

Carbon.	Anthracitic.	Carbonaceous.	Bituminous.			Lignitious.	
			Meta.	Ortho.	Para.	Meta.	Ortho.
	Carbon over 93·3 per cent.	93·3–91·2	91·2–89·0	89·0–87·0	87·0–84·0	84–80	80–75
Per-bituminous genus (hydrogen over 5·8 per cent.).	..	..	Per-bituminous (per-meta-bituminous).	Per-bituminous (per-ortho-bituminous).	Per-bituminous (per-para-bituminous).	Per-lignitious.	
Bituminous genus (hydrogen, 5·0 to 5·8 per cent.).	..	Pseudo-bituminous species.	Meta-bituminous.	Ortho-bituminous.	Para-bituminous.	Lignitious. (Meta).	(Ortho).
Semi-bituminous genus (hydrogen, 4·5 to 5·0 per cent.).	..	Semi-bituminous species (ortho-semi-bituminous).	Sub-bituminous (sub-meta-bituminous).	Sub-bituminous (sub-ortho-bituminous).	Sub-bituminous (sub-para-bituminous).	Sub-lignitious. Meta.	Ortho.
Carbonaceous genus (hydrogen, 4·0 to 4·5 per cent.).	Semi-anthracitic series.	Carbonaceous species (ortho-carbonaceous).	Pseudo-carbonaceous (sub-meta-bituminous).	Pseudo-carbonaceous (sub-ortho-bituminous).	Pseudo-carbonaceous (sub-para-bituminous).	..	..
Anthracitic genus (hydrogen under 4 per cent.).	Ortho-anthracite.	Pseudo-anthracite (sub-carbonaceous).	Pseudo-anthracite (sub-meta-bituminous).	Pseudo-anthracite (sub-ortho-bituminous).	Pseudo-anthracite (sub-para-bituminous).	..	..

N.B.—The various genera are arranged in Column I. vertically according to the hydrogen. The species in each genus are arranged horizontally according to the carbon.

The C/H limits theoretically possible for the various coals of Seyler's classification are appended.

TABLE XIII.—C/H Limits for Various Coals.

Species.	Possible Units of C/H Ratio.
Anthracitic Genus.	
Ortho-anthracite,	23·3 and over.
Pseudo-anthracite—	
Sub-carbonaceous,	22·8 ,,
Sub-meta-bituminous,	22·25 ,,
Sub-ortho-bituminous,	21·75 ,,
Sub-para-bituminous,	21·0 ,,
Sub-meta-lignitious,	20·0 ,,
Sub-ortho-lignitious,	18·75 ,,
Carbonaceous Genus.	C/H Ratio.
Semi-anthracitic,	20·7 to 24 ?
Ortho-carbonaceous,	20·3 to 23·3
Sub-meta-bituminous,	19·7 to 22·8
Sub-ortho-bituminous,	19·3 to 22·2
Sub-para-bituminous,	18·7 to 21·75
Sub-meta-lignitious,	21·0 to 17·8
Sub-ortho-lignitious,	16·6 to 20·0
Semi-bituminous Genus.	
(Anthracitic),	18·7 to 21·2 ?
Ortho-semi-bituminous,	18·2 to 20·7
Sub-meta-bituminous,	17·8 to 20·3
Sub-ortho-bituminous,	17·4 to 19·7
Sub-para-bituminous,	16·8 to 19·3
Sub-meta-lignitious,	16·0 to 18·7
Sub-ortho-lignitious,	15·0 to 17·8
Bituminous Genus.	
(Anthracite),	16·1 to 19·0 ?
Pseudo-bituminous,	15·7 to 18·6
Meta-bituminous,	15·3 to 18·2
Ortho-bituminous,	15·0 to 17·8
Para-bituminous,	14·5 to 17·4
Meta-lignitious,	13·8 to 16·8
Ortho-lignitious,	12·9 to 16·0
Per-bituminous Genus.	
(Anthracitic),	13·9 ? to 16·2 ?
(Carbonaceous),	16·1 and less
Per-meta-bituminous,	15·7 ,,
Per-ortho-bituminous,	15·3 ,,
Per-para-bituminous,	15·0 ,,
Per-meta-lignitious,	14·5 ,,
Per-ortho-lignitious,	13·8 ,,

We feel that any classification which ignores the presence in coal of nitrogen and of a definite amount of water, or which is based solely on the figures of "ultimate" analysis, has no claim to be considered as having a sound philosophical basis. In making this statement we have no wish to deprecate the practical utility of the classifications which have been proposed, but we hope that some more rational classification, based (1) on the composition of a coal itself, and not of an imaginary "substance," of which water and mineral matter are simply the accompanying "accidents"; (2) on the behaviour of the coal to reagents or solvents; and (3) on its behaviour when heated to known temperatures, may in time be adopted. Before leaving the question of ultimate analysis, we must express regret that we are unable to suggest any method of stating the results of such analysis which appears to us to be logical.

Examination of Coke, Briquettes, etc.—This is, generally speaking, carried out in the same manner as has been described for coal, although it may be necessary to modify the examination if the composition of an artificial—*i.e.*, a manufactured—fuel is required.

We have had occasion to examine coal briquettes which were found to consist of small coal mixed with coal-tar. In this case the odour was sufficient to indicate the lines on which the usual examination should be extended, and we found that an extraction with cold carbon bisulphide was sufficient to enable us to obtain the necessary information.

It is unfortunate that a uniform method of expressing the results obtained from the examination of coals has not been adopted, as the omission to do so has precluded the fullest use being made of the very great amount of work which has been done.

In addition to this diversity of expression, many analysts prefer to use methods which are not always recognised by others as being the most satisfactory; it is probable that this is because they have used them for a long period, and that for comparative purposes they prefer to make no departure from them. This, so far as they are concerned, is a perfectly legitimate view to take, but if at any time a question should arise as to different results being returned by other workers, the whole matter becomes confused, and many commercial men can hardly be blamed for inferring that the analytical results were of doubtful value.

Such occurrences would be less frequent, and would be better explained, if the methods adopted for the different determinations were quoted in the report of the analysis. We do not intend these remarks to apply usually where a definite chemical element or compound is to be determined; in such cases the analyst would state the amount of such substance without qualification. Our view is that when dealing with the so-called proximate analysis (since it is not one, as we have stated in a previous chapter, but a usual quantitative record of the behaviour of coal when treated in a particular manner), a statement as to the methods used for determining the moisture and the volatile organic matter would materially assist in solving questions arising from dissimilar results obtained from other sources.

The published results of analyses sometimes consist of a proximate analysis only, an ultimate analysis only, in some cases of portions of each, and in others a proximate and ultimate analysis, with or without the calorific value of the coal.

In some cases we have seen results published giving the composition of the *dry* coal, and no indication of the amount of moisture present in the sample. This is a serious omission, as obviously one does not buy dry coal, and the amount of moisture is, or should be, one of the most important considerations in purchasing coal.

The information given, despite the different modes of expressing the analytical results, may often be sufficient to enable others, experienced in fuel examination, to arrive at the general character of the sample, but to less experienced people the information may be so expressed as to involve them in doubts and difficulties; whereas, by a little readjustment in reporting, the whole could be made readily intelligible.

It is within our knowledge that differences of as much as 2 per cent. in the moisture have been obtained by different workers with the same sample of coal, and as this determination is necessary for obtaining the amount of volatile organic matter, the latter figure would obviously be affected to this extent by the error in the moisture determination. Again, the determination of the total volatile matter, unless made under definite conditions, is likely to give results which might easily increase the error already noted.

We suggest that the subjoined method of stating the results of the proximate analysis, which is a slight amplification of that most frequently employed, would be free from ambiguity, and

TABLE XIV.—ANALYSIS OF COALS.*

	1	2	3	4	5	6	7	8	9	10	11	12
Carbon, . .	62·55	65·50	68·64	69·50	72·14	73·77	74·99	74·57	77·00	76·71	78·80	85·70
Hydrogen, .	3·87	4·23	4·33	4·42	4·40	4·55	4·66	4·74	4·51	4·67	4·92	2·97
Sulphur, . .	1·62	0·67	1·33	0·67	0·61	0·41	0·55	0·47	0·78	0·73	0·50	0·62
Water, . .	8·63	7·92	8·96	9·28	8·34	7·99	7·21	6·95	2·31	1·94	2·72	3·15
Ash, . .	11·78	10·15	6·90	5·97	4·22	1·76	2·68	1·37	7·17	8·49	4·18	3·59
Oxygen and nitrogen,	11·55	11·53	9·84	10·16	10·29	11·52	9·91	11·90	8·23	7·46	8·88	3·97
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
Coke, . .	61·74	61·06	57·53	59·12	58·47	56·93	56·59	56·84	74·61	72·32	66·43	92·03
Fixed carbon, .	49·96	50·92	50·63	53·15	54·25	55·17	53·91	55·47	67·44	63·83	62·25	88·44

The proximate compositions, although not given in the paper, may be readily calculated from the above figures. We give them below.

	1	2	3	4	5	6	7	8	9	10	11	12
Moisture, .	8·63	7·92	8·96	9·28	8·34	7·99	7·21	6·95	2·31	1·94	2·72	3·15
Volatile matter,	29·63	31·01	33·51	31·60	33·19	35·08	36·20	36·21	23·08	25·74	30·85	4·82
Fixed carbon, .	49·96	50·92	50·63	53·15	54·25	55·17	53·91	55·47	67·44	63·83	62·25	88·44
Ash. . .	11·78	10·15	6·90	5·97	4·22	1·76	2·68	1·37	7·17	8·49	4·18	3·59
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

1. Splint coal, Lochgelly, Fife.
2. Boiler fuel (a mixture), Fife.
3. Ell coal, Bothwell.
4. Main coal, Bothwell.
5. Pyotshaw coal, Bothwell.
6. Dunfermline splint, Cowdenbeath, Pit 10.
7. Splint coal, Bothwell.
8. Dunfermline splint, Cowdenbeath, Pit 7.
9. Boiler fuel, Aitken Pit, Kelty.
10. Haughrigg coking coal, Kilsyth.
11. Coking coal, Kilsyth.
12. Anthracite, Kilsyth.

* Gray and Robertson, *Journ. Soc. Chem. Ind.*, 1904, p. 704.

would, in conjunction with the total sulphur and calorific value, be sufficient for all ordinary purposes.

TABLE XV.—Proximate Analysis.

Moisture (determined..............),		10·00
Dried coal	Volatile matter (by................... method),	20·00
	Fixed carbon,	62·00
	Ash,	8·00
		100·00

Total sulphur,	......%
Calorific value of coal as received,	......
,, dried coal,	......

Remarks as to—

Appearance and properties of coke.

,, ,, ,, ash.

The analyses of different samples of fuel in Table XIV. are taken from a paper by Gray and Robertson, *J.S.C.I.*, 1904, p. 704, and give a good general idea of the variations in composition of different classes of coal.

PART II.

CALORIMETRY.

CHAPTER V.

INTRODUCTORY.

I. **Preliminary**—Distinction between Calorimetry, Thermometry, and Pyrometry—Fundamental Interval—Requirements for a Thermometric Substance. II. **Historical Sketch of Thermometry**—(1) Cubical Expansion of Fluids, Gases or Liquids—Thermometric Scales—Effect of Barometric Pressure on Boiling Point of Water—Alteration of Zero—Practical Advantages of the Mercurial Thermometer—(2) Elasticity of Gases—The Air Thermometer—(3) Electrical Resistance Thermometers—(4) Thermo-electric Thermometers—Pyrometry. III. **Objects of Calorimetry**—Change of State—Latent Heat—Specific Heat—Heat of Combustion—Heat of Formation—Principle of Initial and Final States—Gross and Net Calorific Power. IV. **Calorimetric Measurements**—(1) The Method of Mixtures—(2) Isothermal Method—Units—Variation of Specific Heat of Water.

CALORIMETRY—I. Preliminary.—The exact meaning of the word calorimetry and its relation to the etymologically similar words, *thermometry* and *pyrometry*, may well be considered.

Distinction between Calorimetry, Thermometry, and Pyrometry.—Thermometry and pyrometry are operations having for their object the measurement of *temperature*, while *Calorimetry* is the measurement of the *amount of heat change associated with any defined chemical, physical, or mechanical action.*

Temperature, hotness or degree of warmth. Our popular and unsystematic conception of temperature is primarily organoleptic or dependent on the *sense* of warmth. Although it is usually relative, there is a scientific conception of absolute temperature. We may define temperature as *the sensible heat effect produced* *by increments or decrements of heat (or energy) in a system which is not undergoing change of state.* The meaning of this definition may be made more apparent by examples.

We may place a small Bunsen burner or other suitable continuous source of heat under a vessel containing water with ice in it. If the vessel is suitably agitated no continuous change of temperature occurs until the ice is all melted—that is, the increments of heat undoubtedly imparted by the flame have been occupied in doing other work than raising the temperature; they have been so acting on the solid ice particles as to produce the liquid form of the substance—water. The system has been undergoing change of state, and so long as the solid and liquid phases are together present there is no change of temperature. When the solid phase has all disappeared the temperature, as ascertained either by the sense of warmth or by more exact means, steadily rises until a point is reached when change of state again occurs. The water boils, and the liquid and vaporous states are co-existent. The temperature remains constant until all the liquid phase has disappeared, when again the temperature of the system—now steam only—can rise indefinitely.

We can see a similar but reversed change if some liquid glacial acetic acid be placed in a bath of ice water. The temperature speedily falls, and then either remains stationary or rises and then remains stationary until the liquid has become a solid mass. In each of these cases we have seen that heating or cooling is arrested at the point of change of state, and cannot again start until the whole of either the solid or liquid phase has disappeared; although obviously heat is being added to or taken from the system. This heat has been either (1) absorbed in overcoming the resistance of the particles to that change of state which involves their separation—*e.g.*, from ice to water or water to steam—or, conversely, is given out in a change which allows them to do work by coming closer together. Such heat not registered by the thermometer as sensible heat is called *latent heat.* Its amount can be determined by calorimetry, and is a measure of the energy required for, or evolved by the change according to its direction.

Frequent experiment has taught us that *the melting point of ice* and the *boiling point of water* afford fixed points, which by observing certain simple precautions can be reproduced with exactitude. The melting point is practically unaffected by variations of atmospheric pressure; the boiling point is more sensitive, and the fixed point chosen as normal is obtained only when the barometric pressure is 760 mm. (29·92 inches).

Fundamental Interval.—The ubiquity of water and the ease with which it can be obtained in a high state of purity have led to the range between these two points of change of state of water being adopted as the FUNDAMENTAL INTERVAL (F.I.) of thermometry, to which all measurements of temperature are referred. The adoption of such an interval as a standard presupposes the existence of means of measuring temperature, as the bare conception of a standard is, in itself, of no practical use.

Requirements for a Thermometric Substance.—*For the accurate measurement of temperatures we must utilise some substance or system of substances which within our required range suffers no change of state,* and so far as may be has an unvarying capacity for heat, and has some property which suffers alteration bearing a definite and preferably simple relationship to the increment of temperature. We may here usefully consider some proposals which have been made for the measurement of temperature.

II. Historical Sketch of Thermometry.—(1) **The cubical expansion of fluid** appears to have been the first property to be utilised for the purposes of thermometry. Early in the sixteenth century it would appear that both Santorio (Sanctorius) of Padua and Cornelius Drebbel of Alkmaar in Holland used the air thermometer, and the former* claimed the invention. A strong claim is made for Galileo; probably all three workers made independent discoveries. Robert Boyle (d. 1691), Amontons (1702), and others improved this instrument, which is still, in fact, the ultimate court of appeal in the matter. Very early, however, the fact was realised, which is now only too apparent, that for a working instrument the air thermometer is too troublesome. The difficulties of the early workers were not those which present themselves to their successors, but they were due rather to variations of the pressure of the atmosphere and of the column of confining liquid than to the deformation and porosity of the substances used for the envelope or container which have troubled modern workers.

About the middle of the seventeenth century the members of the Accademia del Cimento, instead of confining a volume of air in a bulb with a long, narrow neck and measuring differences of temperature by the travel of the surface of contact between

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* *Commentaries on Avicenna*, 1626.

the air and its liquid confining medium in the long tubular neck, reversed the construction, and filled the bulb and part of the neck with alcohol, expelling the air above the spirit by boiling, and sealing off the end of the tube. Robert Boyle introduced the instrument into this country. It was soon found that, although the spirit thermometer could apparently be used at the very lowest temperatures, its upper range was not high, and it was not suitable for temperatures much higher than those obtained in meteorological observations. Sir Isaac Newton, dissatisfied with the range of the spirit thermometer, used linseed oil; in fact, his well-known law of cooling, to which reference will be made later, was worked out with a linseed-oil thermometer. Although linseed oil offers a fair range of temperature without change of state, its viscosity and surface tension are high, and the substance of a thermometer when the temperature was falling was found so to adhere to the sides of the tube as to reduce greatly the accuracy obtainable. The astronomer Halley appears to have been the first to suggest that mercury was a very suitable fluid for use in thermometers, but he seems to have been discouraged by its low coefficient of expansion relative to alcohol. Boerhaave * ascribed the invention of the mercurial thermometer to Römer in 1709, but the first mention of it in this country is in the *Philosophical Transactions*,† when a thermometer designed by Fahrenheit, of Amsterdam, in 1820, was described.

Fahrenheit's instrument was practically the same as is used to-day; the many improvements which have been made have in no wise affected the general principle.

Fahrenheit appears to have made use of the fundamental interval for the division of his thermometric scale, although this is not certain, nor is the real meaning of his zero point—32 of his degrees below the melting point of ice—known. The fundamental interval in his thermometer was $212 - 32 = 180$ degrees.

Newton and Boyle graduated their thermometers on the basis of a definite fraction of the volume of the oil when immersed in ice. The latter worker used the ice point, blood heat, and the boiling point of water as fixed working points.

The scale known as Réaumur's, which, in fact, is rather Deluc's, is based on $\frac{1}{80}$ of the fundamental interval.

Celsius, of Upsala, a Swede, towards the end of the eighteenth century, made the convenient suggestion that the fundamental

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* *Elementa Chemia*, 1732.

† Vol. xxxiii., 1724.

interval should be divided into 100 parts. His scale and Fahrenheit's are used to-day to the exclusion of all others.

Effect of Barometric Pressure on Boiling Point of Water.—Fahrenheit in 1824 noticed that the pressure of the atmosphere caused a variation in the temperature at which water boils, and Deluc suggested a formula connecting these variations. Bird, an English scientific instrument maker, seems to have been the first actually to use a correction in graduating thermometers, and in 1776 the Royal Society appointed a Committee to consider the best means of adjusting the fixed points of thermometers. Sir George Schuckburgh gave the following correction for determining the true place of the boiling point of water :—

28-inch barometer, ...	− 3·48° F.	Correction to be applied to 212° F.
29-inch ,, . .	− 1·72° F.	
30-inch ,, .	0·0° F.	
31-inch ,, ...	+ 1·69° F.	

The committee noted that the whole of the mercurial column, as well as the bulb, should be heated or cooled to the temperature of the fixed point, or, if this cannot be done, a correction should be made.* It will be seen that a height of 30 inches of mercury was adopted as the normal barometric pressure. The 760 mm. point now adopted for the standard pressure is equal to 29·92 inches, and the difference between these two points corresponds to about 0·14° F.

It must be borne in mind that all thermometers dependent on the expansion of fluids are non-homogeneous in composition, since they are made with an envelope and tube which has not only a capacity for heat and coefficient of expansion, but is liable to alteration of form.

What is actually measured in either a gas or liquid thermometer is not exactly the expansion of the gas or liquid, but the excess of this over the expansion of the container or envelope. The fact that this excess is always very large does not altogether do away with the circumstance that variations in the regularity of expansion of either envelope or fluid cause the degrees as indicated to be either greater or less than the nominal fraction of the fundamental interval which they are intended to represent.

Alteration of Zero.—The bulb of a thermometer is fashioned at the high temperature required for the partial fusion of the envelope, usually, in mercurial thermometers, glass, and it is

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* *Phil. Trans.*, vol. lxvii.

a very long time before it contracts to a constant volume. Even when this contraction has occurred a temporary depression of zero consequent on expansion and retarded contraction will be noticed if the thermometer is raised to a high temperature and the ice point taken soon afterwards. Modern improvements have been directed chiefly to the manufacture of glasses which shall be as satisfactory as possible in the above particulars, and in certain others which will be referred to later.

That the expansion and contraction of a thermometer bulb is really appreciable can be easily shown by dipping a thermometer, preferably with a large globular bulb, into a vessel of water several degrees colder than the bulb. The mercury at first rises in the tube and then very quickly falls; the contraction of the bulb occurs before that of the mercury, and so squeezes it up the tube. The converse occurs when the bulb of a cold thermometer is grasped by the hand. A thermometer belonging to one of us was plunged into cold water when indicating a temperature of 20·0°. The mercury rose to 20·2° and then fell to 9·0°. When taken out and grasped it fell to 8·9° and then rose.

Practical Advantages of the Mercurial Thermometer.—It may be said that notwithstanding its many defects the mercurial thermometer is the most convenient instrument for many practical scientific purposes within reasonable limits of temperature. The obvious limits are those at which change of state occurs. Mercury solidifies at $-37 \cdot 7°$ C. and boils (under 760 mm. pressure) at 357° C.* Distillation in the thermometer tube occurs below this temperature. Still it might reasonably be considered that the effect of heat in separating the particles and causing the expansion of mercury would be constant for very nearly the whole of this range. This is not actually the case, since mercury does not comply exactly, although very nearly so, with the requirement of having an unvarying capacity for heat. In fact, the only bodies complying very rigidly with this requirement are the so-called perfect gases, and of these the most suitable for thermometric purposes are those which are with the greatest difficulty induced to undergo change of state, such as hydrogen, nitrogen, and helium.

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* Mercurial thermometers having envelopes of special borosilicate glass (Jena 59^{III}), and with the usually vacuous space above the mercury filled with nitrogen, are made for use up to 550° C. This should only be done when convenience is considered more essential than accuracy. The mercurial thermometer is not the best form of pyrometer.

(2) **The elasticity of gases** is more conveniently measured than their expansion, and the very wide range through which gases manifest a constant ratio between the increment of elasticity and the increment of temperature makes the gas thermometer very accurate for all temperatures above the critical temperature of the gas used.

The Air Thermometer.—The relative simplicity of the molecules of gases is in their favour for this purpose, but, on the other hand, the gas thermometer, owing to the many practical difficulties of using it, is suitable only for a standard, and not as an instrument for every-day work.

The very low compressibility of liquids renders this method of estimating the effect on them of heat quite outside the scope of practical thermometry. Expansion methods only are applicable to them.

We do not think that it is likely that the gas thermometer would be used in any of its best known forms for ordinary calorimetry. Strache's gas calorimeter is the only practical appliance in which we remember this principle to be used, and the arrangement there is hardly a thermometer in the usually recognised sense.

(3) **The Electrical Resistance Thermometers.**—*The electrical resistance of a platinum wire* increases in an almost linear relationship to the temperature. Sir W. Siemens (Bakerian lecture, 1871) proposed that this fact should be utilised for practical thermometry of high temperatures, but an adverse report of a Committee of the British Association led to the neglect of this method. Callendar and Griffiths, who had previously independently investigated this principle of measurement, introduced (1892) a platinum resistance thermometer suitable for any temperatures up to about 1,400° C., and equally suitable for measurements of small differences amounting only to thousandths of a degree.

Of all electrical measurements, that of resistance is the most exact, and as the relationship of the variation with that of temperature has been well investigated, the principle offers peculiar advantages when exact measurements are of more importance than great ease of manipulation, or rather perhaps than the entire absence of manipulation, although very simple indicating or recording appliances of this kind are now made, and for high temperatures are used in technology.

(4) **Thermo-electric Thermometers.**—If two metals are connected in an electric circuit in such a way that one junction

between them is hotter than another similar junction, a difference of electrical potential is observed between them which bears a definite relationship to the difference of temperature. This thermo-electric effect was first noted in 1822 by Seebeck, with the metals bismuth and antimony. Becquerel, in 1826, proposed this as a means of measuring high temperatures, and Melloni, in 1850, published (*La Thermochrôse*, Naples) his researches on radiant heat, in which he used a thermo-pile or series of thermocouples as a delicate and rapidly indicating thermometer.

After much work on the part of many observers, Le Chatelier, in 1886, introduced a really efficient thermo-electric thermometer for high temperatures, in which the metals were platinum and an alloy of 90 per cent. platinum and 10 per cent. rhodium used with a d'Arsonval moving-coil mirror galvanometer. Since that time various combinations of metals have been used with great success, either for the approximate and rapid measurement of high temperatures or for the more exact measurement of ordinary temperatures. The relation between temperature and electromotive force has been carefully studied in these cases, and formulæ of greater or less accuracy have been proposed as connecting these variables.

For the temperatures measured in practical calorimetry, copper-constantan (copper 60 per cent., nickel 40 per cent.) or iron-constantan couples or series of couples have been used, and are suitable.

All the methods above described are, with greater or less convenience, suitable for the measurement of ordinary temperatures. The mercurial thermometer, as we have seen, is only suitable for measurements below 360° or, under certain circumstances, 500°. The temperatures for which the other methods are available are only bounded on the one hand by the approach of the air or other gas used in the gas thermometer to its liquefying point, and of the more fusible metals used in thermo-couples or the platinum wire of a resistance thermometer to their melting points. We thus get a range of from, say, $-270°$ C. to $+1,750°$ (actually 1,400 is about the limit of platinum or platinum-alloy thermometers).

Pyrometry may be considered a more suitable name than thermometry, or, at any rate, a more descriptive one, when we begin to get outside the range of the mercurial thermometer; and the platinum and thermo-electric thermometers when used for such temperatures are more commonly known as pyrometers.

Other methods of temperature-measurement, which are only available for temperatures above a red heat, come within the scope of pyrometry rather than thermometry. Among the most important are the various forms of radiation pyrometers, some of which, such as Féry's, are based on the measurement of the total radiation from a heated inclosure (the black body of Kirchoff) and others, such as the optical pyrometer of Holborn and Kurlbaum, on the measurement of the intensity of some selected ray.

The scientific and industrial importance of measurements of temperature can hardly be over-estimated, and many of the advances in such industries involving the use of high temperatures as the smelting and working of iron and other metals, are due to the results of researches which at the time appeared to be of purely theoretical interest.

It is perhaps obvious that the effect of the addition, to any such direct thermometric system as we have supposed, of energy in the form of heat will be most nearly proportional to the amount of energy added, when the range which has to be considered is very small in proportion to that represented by the limits of state of the system; and that, therefore, the best materials for thermometers are either perfect gases or solids of very high melting point. This superiority is, in practice, less marked when the range in an experiment is very small as, for this and other reasons, is always the case in good calorimetric work. So that, in fact, first-class mercurial thermometers are good enough for almost all work, the principal objection to them being that some patterns have a rather high "lag"—that is, a slow rate of change of temperature—a defect shared with some forms of platinum-resistance thermometers—*e.g.*, Callendar's.

For calorimetric purposes the mercurial thermometer is most often used, although work of the highest kind has been done with both the resistance thermometer and the thermo-couple, and no doubt the tendency to use these is on the increase.

III. Objects of Calorimetry.—Calorimetry, although in most cases dependent on thermometry, involves a wider conception. It is the measurement of the energy accompanying physical or chemical change, which is manifested as an evolution or absorption of heat. We may well consider some of the various classes of measurements which come under the category of calorimetry; first, *physical measurements.*

Change of State.—We have seen that in the liquefaction of ice a continuous absorption of heat takes place. The amount of this absorption has been measured by inducing the change under accurately recorded conditions and noticing the alteration of these conditions due to it. We can measure by appropriate means the heat effect produced by evaporation of water, which is, like that of the melting of ice, negative in sign, or that produced by the condensation of steam, which is positive in sign, but in amount equal to that of evaporation.

Latent Heat.—Black, in 1762, was the first to observe and measure both the latent heat of water and that of steam. He employed the method of mixtures mentioned below, which is still most often used in calorimetry. These values have been the subject of work by many physicists, notably, for ice, Person (1850), Regnault (1862); and for steam, Regnault (1847), Andrews (1849), Favre and Silbermann (1853), down to Richards (1911). Some of the best values may be given here, it being noted that the value of the unit—the calorie—will be discussed later.

TABLE XVI.—LATENT HEATS (15° CALORIE).

Ice-Water.		Water-Steam.	
Regnault,	79·25	Favre and Silbermann (at 98·81°).	535·77
Person,	79·25	Andrews (at 100°),	535·9
Bunsen,	80·025	Regnault (whole heat, 100° to 0°),	637·0
Desains,	79·24	Berthelot ,,	636·2
Smith,	79·91 ± ·02	Smith,	539·0
		Richards,	538·0

Specific Heat.—Another class of purely physical measurement is that of the capacity for heat of various substances—*i.e.*, their *specific heats*, or the relative amounts of heat required to warm or cool unit weights through unit temperature.

All these measurements—the latent heat of liquefaction, vaporisation, and the specific heat—have for the same substance and the same conditions definite values, which, when determined, vary only within the limits of experimental error.

Values for the specific heats of various substances can more usefully be given later in the next chapter. The principal early workers in this direction have been Regnault (1840-63), Favre and Silbermann (1852), and Dulong and Petit.

Heat of Combustion.—That a manifestation of energy in the form of heat accompanies chemical change is well known. Without considering any recondite chemical reactions, it will be remembered that a very great part of our ideas of heat are centred round that of the very well known chemical change of combustion, and that the study of certain results of this particular change is the object of this work.

The first attempts at measuring the heat of combustion of substances were made by Lavoisier and Laplace in 1780. They used an ice calorimeter, based on the principle of change of state mentioned below. The ever practical Count Rumford, desiring to know the relative values of various fuels, applied Black's method of mixtures to these measurements in 1814. Andrews (1848), Favre and Silbermann (1852-3), Julius Thomsen (1853), and Marcelin Berthelot (1894) devoted their attention to thermo-chemistry, and particularly to heats of combustion. Other less prominent workers have made valuable contributions to our knowledge of these values.

Combustion is distinctly a change of an *exothermic* character—that is, it is one in which heat is evolved. There are other changes which we do not at present need to consider, which are only brought about by the absorption of heat. Such are called *endothermic.*

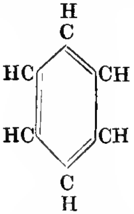
A most important question, involving the validity of chemical calorimetry and of thermo-chemistry, is whether the manifestation of energy as heat, accompanying a chemical change, is constant in amount for that change.

For example, if we determine the heat of combustion of carbon, shall we get the same value if we redetermine it? It is to be feared that the answer, for most of us, is "probably not," since experimenters, unlike poets, are made, not born; or, perhaps, both poets and experimenters are born, more or less as such, and then achieve proficiency in their respective arts by training and experience. Carefully conducted experiments have shown that such values as that mentioned are constant, for the substance in the same form, within limits which it is reasonable to ascribe to experimental error, which limits, even in the best work of this kind, are not as small as could be wished. The following are a few values found for the heat of combustion of 1 gramme molecular weight of carbon—*i.e.*, 12 grammes :—

C (amorphous) 2 (O),	+ 96·96	Calories	(Thomsen).
„	+ 97·65	„	(Berthelot and Petit).
C (graphite),	+ 94·8	„	(„).
C (diamond),	+ 94·3	„	(„)

It is worthy of note that this and other similar values are constant, irrespective of the method of determination, provided it is free from adventitious errors. The differences between the values for diamond, graphite, and amorphous carbon are marked. One obvious reason suggests itself—the physical conditions of the three forms are different and, therefore, the energy to be overcome by the chemical change is likely to be different in amount. Similarly, the heat of combustion of the same substance in solid and liquid states is different, owing to the differences of energy required in effecting the physical change.

Again, the heats of combustion of substances of the same percentage composition, but in which the atoms are differently arranged, are different. We may consider benzene and its isomer.



Benzene, (799·3)

$CH : C . CH_2 . CH_2C : CH$

Dipropargyl (882·9).

It will be seen that both these values are different from those obtained by calculation from the heats of combustion of carbon and hydrogen.

$$\begin{array}{lcll} 6\ C,O_2 & = & 6 \times 96{\cdot}96 \text{ Calories} & = 581{\cdot}76 \\ 3\ H_2,O & = & 3 \times 69 \quad\quad ,, & = 207{\cdot}0 \\ \hline & & & \ 788{\cdot}76 \end{array}$$

In each case more heat is evolved by the combustion of the hydrocarbon than might be expected. It must come from somewhere. The reasonable explanation is that the formation of each of these compounds involves an absorption of heat—that is, they are *endothermic*, and their mere decomposition will give rise to an evolution of heat irrespective of that produced by the combustion of their elements.

Heat of Formation.—We see, therefore, that the heat of combustion, to keep to our special case, is determined for each substance, not only by its ultimate chemical composition, but by its constitution—that is, for each substance a definite amount of heat is required or evolved for its formation, and when it is decomposed—apart from any other heat changes due to new combinations of its liberated constituents—the same amount of heat is either evolved or absorbed.

The heat of formation of a combustible substance is not usually a value which can be determined by direct means, but heats of combustion usually can, and it is this class of measurements which is properly comprised under the term fuel calorimetry.

Apart from the above purely chemical considerations affecting the actual heat of combustion of a substance, the condition of the *end products* affects this value.

For example, the following figures for the heats of combustion of hydrogen and of sulphur show how latent heat modifies the final result :—

	Gas.	Liquid.	Solid.	
2 (H) + O (at 0°)	+ 58·1	+ 69·0	+ 70·4	Berthelot and Matequin.
(S) + 2 (O)	71·1	77·3		Thomsen.

Principle of Initial and Final States.—Berthelot expresses the principle, a corollary from the first law of thermo-dynamics, on which the whole of thermo-chemistry is based, as follows :—

"If a system of simple or compound bodies taken under determined conditions experiences physical or chemical changes capable of giving rise to a new state without exerting any mechanical effect exterior to the system, the quantity of heat disengaged or absorbed as an effect of these changes, depends solely on the initial and final states of the system; it is the same whatever the nature and the sequence of the intermediate states."

In considering the combustion of fuel of the kinds used in industrial operations, we have a restricted case for the application of this principle. The fuel is always in a definite physical state, and is used in that state. The products are simple, water and carbon dioxide, or steam and carbon dioxide, with little more than traces of other substances. So that we have the scheme—

$$\text{Fuel} \left\{ \begin{matrix} \text{Solid,} \\ \text{liquid, or} \\ \text{gas} \end{matrix} \right\} + \text{oxygen} = x\text{H}_2\text{O} + y\text{CO}_2.$$

It is immaterial to us so long as we obtain these products of complete combustion, what the mechanism of combustion is, whether a preferential combustion of hydrogen or of carbon or a process of hydroxylation takes place; but it is very important that the carbon shall all be burnt to CO_2 and none escape as CO.

The combustion of 12 grammes of carbon may be regarded as involving—

(1) The conversion of solid carbon into "atomic" carbon, in which change heat is absorbed by the system;

(2) The combustion of this to CO, in these two changes the heat effect is the evolution of 29 Calories;

(3) The combustion of CO to CO_2, in which 67·96 more Calories are evolved.

This view is based on the fact that—

$$\begin{array}{lrl} & C + O_2 = CO_2 + 96{\cdot}96 & \text{Calories.} \\ & CO + O = CO_2 + 67{\cdot}96 & \text{,,} \\ \cline{2-2} \text{Therefore,} & C + O = \quad 29{\cdot}00 & \text{,,} \end{array}$$

And as it is reasonable to suppose that the union of each atom of O to carbon is accompanied by a similar evolution of heat, and that the difference between 2 × 67·96 = 135·92 and 96·96 must equal the heat of formation of the carbon atom from solid carbon.

From the fuel point of view, the matter of chief importance is that in burning carbon we get 96·96 Calories, and not merely 29·00—*i.e.*, that combustion is complete.

In the case of the hydrogen no possibility of incomplete combustion to a suboxide is known, although, in fact, when fuel containing both carbon and hydrogen, as all coal or oil, or gas obtained directly from these materials does, is burnt, hydrocarbon gases do sometimes escape from industrial furnaces. In almost all cases, when examining fuel, it is both easier and better to make a direct determination of the heat of combustion than to try to calculate it, since to do the latter with accuracy it is necessary either to have a full knowledge of the nature and heats of combustion of all the proximate constituents of the fuel, or to know the ultimate composition and the heat of formation of the substance under examination. It is seldom that either of these conditions is fulfilled, and the various attempts at compromise which have been made cannot be regarded as successful. The automatic integration of all the values concerned, which is afforded by careful combustion in a calorimeter, gives results which are far more reliable than any calculation, and is not necessarily a long operation.

Gross and Net Calorific Power.—A point needing consideration as to the product of combustion of the hydrogen has been indirectly indicated. In our process of combustion is the product H_2O to be obtained as water or as steam? and what difference in the value of the fuel will be observed in these cases? Under any ordinary conditions the CO_2 will always be obtained as a gas, and, therefore, need not be considered (except so far as in some forms of apparatus its escaping temperature is concerned), but a definite and considerable amount of heat is expended in vaporising water or is liberated in condensing steam. Whether our combustion is to be considered as taking place under the conditions of a geyser or condensing radiator stove, on the one hand, or of a kettle or a boiler furnace, on the other, is a matter of importance.

The heat of combustion or calorific power realised by cooling the products obtained by burning fuel, so that water is condensed—a condition obtained in most calorimeters—is called the *gross* or higher value, and that corresponding to the escape of water as steam is called the *net* or lower value. This word *net* is misleading, as it gives the impression of being the truer value of the two, and, if we may so express it, the more businesslike. This is not altogether the case, since this value, as obtained, represents no conditions which occur in actual practice, as it is always calculated from the water only, and no regard is paid either to the CO_2 or to the excess of air or oxygen. Its only meaning is as a measure of the hydrogen in the fuel and an indication of the loss, in most practice, due to latent heat; this is only a part, and an indefinite part, of the total loss.

In speaking of the heat of combustion of fuel, we need to understand which value is intended, whether " gross " or " net." When not otherwise stated, the values referred to in this work will be gross—that is, those obtained when the products of combustion are cooled to a temperature approximating to that of the room in which the experiment is carried out.

IV. Calorimetric Measurements.—Having now some idea as to the definite nature of the quantities proposed to us for measurement by calorimetry, and of the ancillary operation of thermometry, we are in a position to consider how these measurements should be made. Two methods appear to be of general application.

(1) **The Method of Mixtures.**—To carry out the operation, the heat effect of which is to be measured, in such contact or

juxtaposition with another substance of known specific heat that the value to be measured may be gauged by the change of temperature produced in the whole system. Here it is apparent that the less the change during the experiment of specific heat in the calorimetric substance, as it may be called, or that which takes the passive part of having the heat communicated to it, the more suitable will it be for the purpose. Obviously the magnitude of this substance may be so adjusted that the temperature change is small, and the possibility of serious variation of heat capacity thus be reduced. This method clearly involves, apart from suitable form of apparatus, etc.—

(a) *A knowledge of the mass of the substance whose change is to be measured.*

(b) *A knowledge of the heat capacity of the calorimetric substance (this is obviously the product of its specific heat and its mass* or, *if not a simple substance, the sum of these products for all its parts).*

(c) *A sufficiently sensitive and accurate thermometer.*

The general course of an experiment of this kind in an ideal system will be (*first*) the production of the change or reaction; (*second*), the interchange of heat until a uniform distribution of temperature is reached. The general expression will be, when M represents the mass of the acting substance and H the heat effect of unit mass to be measured, C the capacity of the calorimetric substance, and T the observed temperature change.

$$M \,.\, H = C\,T \;\therefore\; H = \frac{C\,.\,T}{M}.$$

Note.—T may be + or −.

Perhaps a concrete example will explain this point more clearly.

Suppose we burn 1 gramme of amorphous carbon, and the total capacity of the calorimetric system is = 3,000 grammes of water. The observed temperature change is found to equal 2·705° C.

Then $M = 1.$
$C = 3{,}000.$
$T = 2{\cdot}705°$ C.
$M \times H = 3{,}000 \times 2{\cdot}705.$
$\therefore \quad H = 8{,}115$ grammes of water heated 1° by 1 gramme of carbon.

The vast majority of calorimetric experiments are conducted on this principle, and water is usually used as the calorimetric substance. Other liquids have been proposed for special cases. Favre and Silbermann used mercury, and Nernst, Koref, and Lindemann have recently used a copper block instead of water for very delicate work. Raupp has also used copper in a gas calorimeter. A very ingenious method for determining specific heats at different temperatures has been used by Nernst, who allowed the substance itself to be the calorimetric substance, and imparted the heat for the rise of temperature by electrically heating a platinum wire in it, and measured the temperature by the alteration of resistance of the same wire.

The method of mixture was introduced by Black.

(2) **Isothermal Method.**—An isothermal method not involving thermometry can be used by allowing the acting substance to induce a change of state in the calorimetric substance. Here we need, instead of a thermometer, some means of measuring the amount of substance undergoing the change of state, and an accurate knowledge of the heat effect of the said change. This method, introduced by Lavoisier and Laplace, is less often used than the former, but two types of appliance are used, one on a very small, the other on a very large scale—*e.g.*, Bunsen's (and others') ice calorimeter in which a small amount of reacting substance is allowed to melt ice, the amount melted being measured either by the alteration of volume or by other means: and, secondly, the rough method of valuing fuel used by some engineers in which the *steam raising power* of a known amount of it is measured.

Units.—We now have to consider how to express the heat values when we obtain them. Water has been universally adopted as the standard substance from motives of convenience only, and the amount of heat required to effect the change of the temperature of 1 gramme of water through 1° C. has been adopted as the unit under the name of the *calorie* or gramme calorie. Since, for some purposes, the numbers expressed in this unit are inconveniently large, another calorie, the kilogramme Calorie = 1·000 gramme, or small calories, is often used. This is briefly referred to as the K.G. calorie or the Calorie (with a capital C).

Variation of Specific Heat of Water.—Unfortunately, the calorie, as above described, has been found not to be as definite a unit as could be desired. Regnault, in 1847, investigated the variations with temperature of the specific heat of water, and Rowland, an American physicist, in 1879, found that by working at different temperatures he obtained differing values for the mechanical equivalent of heat, and these differences he rightly concluded to be due to an alteration of the specific heat of water. This he made the subject of investigation. Contrary to the conclusions arrived at by Regnault, he found that *a minimum point* was reached. This point he placed at, or near, 30° C. Since the time of Rowland the subject has been worked at by Bartoli and Stracciati (1893), Griffiths (1900), Lüdin (1900), Callendar and Barnes (1902), W. R. and W. E. Bousfield (1911), Ianke (1911), and Callendar (1912). A brief summary of the methods and results obtained prior to 1911 is given in *The Calorific Power of Gas*, pp. 137-139. It may be well here to give the figures which were then recommended, the mean of Bartoli and Stracciati's and Lüdin's figures for temperatures from 0° to 25° C., and to compare them with the more recent figures of the Bousfields, of Callendar, and of Ianke.

TABLE XVII.—Specific Heat of Water (15° calorie).

	Mean of Bartoli and Stracciati and Lüdin.	Bousfield.	Ianke.	Callendar and Barnes.	
				1902	1912
0°, . .	1·0060	1·0070	1·0068	. .	1·0094
5°, . .	1·0034	. .	1·0040	1·0050	1·0048
10°, .	1·0013	1·0016	1·0016	1·0020	1·0019
15°, .	1·0000	1·0000	1·0000	1·0000	1·0000
20°, . .	0·9993	·9991	·9991	0·9994	·9988
25°, . .	0·9994	. .	·9987	0·9978	·9980
30°, . .	. .	·9990	·9988	0·9973	·9976
40°, . .	. .	1·0006	·9992	0·9971	·9974
50°, .	. .	1·0031	1·0003	0·9977	·9978
60°, .	. .	1·0058	·9992	. .	·9987
70°, .	. .	1·0080	. .	. .	1·0001
80°, .	. .	1·0091	. .	. .	1·0017

It should be stated that Barnes' work in 1902 was carried out in a most thorough manner and, as far as was possible, in collaboration with Callendar, although the circumstance that the Atlantic divided them for greater part of the actual work reduced the effect of this collaboration.

The method used was devised by Callendar, and called by him the continuous electrical method. Heat was imparted to a stream of water flowing through a fine glass tube in a Dewar jacketted vessel by means of a known electric current flowing through a wire passing along the tube, and the temperatures of inlet and outlet water were taken by differential platinum thermometers. By this means the ratio of the amount of electrical energy required to cause a certain rise of temperature between any desired ranges could be determined and, therefore, the ratios of the specific heats of water within the respective ranges of temperature could be deduced.

Callendar,* desiring to verify these results of 1902, which in the upper range differed from those of Lüdin and of Bousfield, designed a new method called by him the "continuous mixture method," of still greater ingenuity than that used in 1902.

A current of water at a steady temperature t_1 in the neighbourhood of 100°, is passed through an arrangement of concentric tubes, called a "heat exchanger," emerging at a measured temperature t_2 in the neighbourhood of 70° After being cooled to a measured temperature t_3 in the neighbourhood of 30°, the same current is passed through the heat exchanger again, abstracting heat from the hot current by conduction without actual admixture, and emerging finally at a temperature t_4 in the neighbourhood of 60°. The errors are by suitable means reduced almost to those of the platinum thermometers, which, for the temperature ranges chosen, are about $\frac{1}{30,000}$ (*i.e.*, ·001°). The current of water cooled from t_1 to t_2 is equal to that warmed from t_3 to t_4, and consequently the temperatures give exact values for the ratio of specific heat between 70° and 100° to that between 60° and 30° The results of about 150 experiments by this method confirmed those previously obtained over this range of temperature to less than 1 in 5,000, whereas the discrepancy from Lüdin's formula exceeded 1 in 200.

It will be noted that in this method the only measurements are those of temperature, and that the relatively weak measurement of electromotive force is entirely eliminated.

Callendar gives the following formula to represent the variations of specific heat between 0° and 200°, in terms of specific heat at 20° as unity :—

$$S = \cdot 98536 + \frac{\cdot 504}{t + 20} + \cdot 0084 \frac{t}{100} + \cdot 0090 \left(\frac{t}{100}\right)^2.$$

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* *Bakerian lecture*, Royal Society, 1912.

The figures in Table XVII. are, for purposes of comparison, all reduced to the basis specific heat of water at 15° = 1, as this appears to be more usually adopted, but, of course, there is no reason, other than that of convenience or personal preference, why this should be. The older conception of the calorie was that it should be the amount of heat required to raise 1 gramme or 1 kilo. of water from 0° to 1° C., but this was found to be considerably different from the value of 1° rise of temperature of water at the temperature more often used in calorimetry. Unfortunately, the *mean calorie* of Bunsen based on the fundamental interval 0° to 100° has not been found to be a practical unit, owing to the difficulty of determining its value. Barnes and Griffiths have proposed 16° and 15° respectively as giving values probably closer to the mean calorie 0° to 100°.

In 1901 Griffiths modified his views, and preferred 17·5° as representing the mean of the range over which very many experiments would be conducted in practice—*i.e.*, 15° to 20°. Callendar prefers to take, as we have seen, 20° as his standard temperature as the mean of the range 15° to 25°, and to consider a range of 10° rather than of 1°.

If the temperature of the minimum were well known, and were a point within the usual range of experiment, it is obvious that this would, as representing the range of slowest change of value, be convenient. It, however, occurs at a temperature not lower than 25°, and probably nearer 40°. It is, therefore, best to adopt one of the temperatures from 15° to 20° as the standard. Having regard to the careful and very thorough work of Callendar, confirming his earlier work with Barnes, we advise the use of his values in all cases where it is worth correcting results for this small source of error, and that it should be made clear in returning important results whether the relative values are referred to his standard temperature of 20°, or to some other temperature. The difference between the 15° and the 20° calories amounts to about 1 in 1,000. There are few calorimetric experiments which would be seriously affected by this error.

The curve (Fig. 30) shows the variation of the specific heat of water according to Callendar's formula, between 0° and 100° C. It will be seen that a minimum occurs at 40°, and that the specific heat afterwards increases to unity at 62°, and then steadily goes up. The very complex nature of liquid water, as we know it, is suggested by these anomalies of specific heat and other anomalous properties of water, and it appears probable that ordinary water is a mixture of hydrol H_2O, dihydrol H_4O_2, and trihydrol H_6O_3, and that the proportion of these varies according to the temperature. A very useful table, a few values from which are to be found in Table XVIII., is given by Callendar.* It shows the increment of heat, *d h*, which should be added to the temperature *t* reckoned from 0° C. to show the total heat,

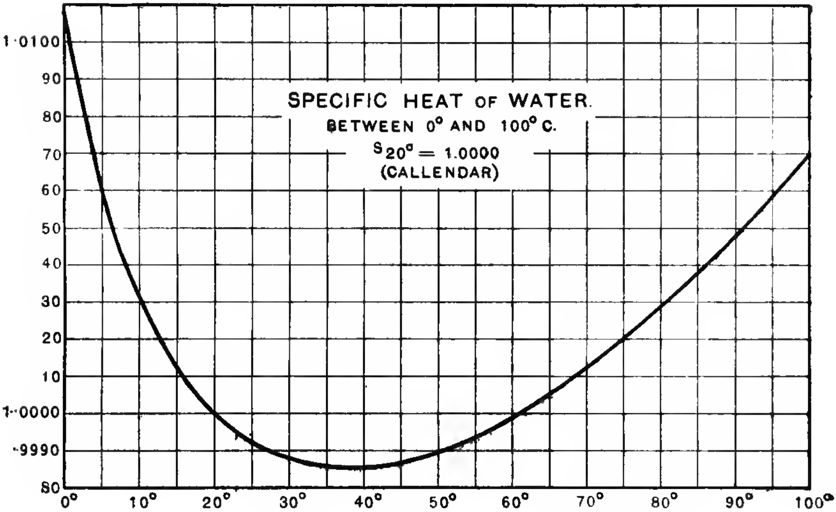

Fig. 30.

$t + d\,h$, between t and 0. Thus the total heat at 10·531° is $10·531 + ·062 = 10·593$, or, more accurately, $10·593 + (·065 - ·062)\,·531$; and at 17·376° C., $17·376 + ·074 = 17·450$, so that the change of temperature of water from one of these temperatures to the other involves a change of

$17·450 - 10·595 = 6·855$ calories per gramme.

and not $17·376 - 10·531 = 6·845$,, ,,

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* *Phil. Trans.*, Bakerian Lecture, 1912, A. 212, p. 31.

TABLE XVIII.

Total Heat of Water (*Callendar*) $= t + d\,h$. $S_{20} = 1{\cdot}000$.
Values of $d\,h$.

	0	1	2	3	4	5	6	7	8	9
0°, .	·000	·010	·019	·027	·034	·040	·046	·051	·055	·059
10°, .	·062	·065	·068	·070	·071	·072	·073	·074	·075	·075
20°, .	·075	·075	·075	·075	·074	·073	·073	·072	·071	·069

In order to avoid large errors due to the variable specific heat of water, it is desirable that, as far as may be, calorimetric experiments should be effected at temperatures near to 15° or 20°, and, as a necessary corollary, that the temperature change in such uncorrected experiments should be only a few degrees.

We can obviously, for any chemical or physical change, connect the amount of heat change in calories with some suitable unit of mass or volume of the substance experimented on, and to obtain a proper expression for the desired value we must do this. In studying, from a purely scientific standpoint, the heat changes accompanying chemical action it is preferable to consider the relative masses of reacting substances and, therefore, to express the values in calories per gramme-molecule, or when the aggregation of the molecule is unknown per gramme-atom. For example,

$$C + O_2 = CO_2 + 96{\cdot}96 \text{ K.G. Calories}$$

means that the combination of 12 grammes (1 gramme-atom) of carbon with oxygen to form 44 grammes of carbon dioxide is accompanied by an evolution of 96·96 K.G. Calories, or 96,960 gramme calories. Again,

$$H_2 + O = H_2O \text{ (liquid)} + 68{\cdot}36 \text{ K.G. Calories}$$

means that 2 grammes of hydrogen uniting with oxygen to form liquid water evolve 68·36 K.G. Calories.

For technical purposes it is more convenient to express the heat of combustion, or calorific power, as it is more usually called in such cases, of *one gramme* of carbon as $\frac{96{\cdot}96}{12}$, or 8·08 K.G. Calories, or 8,080 small calories.

Again, it is unusual to measure gases by weight, and the heat of combustion of hydrogen can more conveniently be considered as that of 1 gramme molecular volume, the same mass (2 grammes) as shown above, which is 22·412 litres at 0° and 760 mm.

Here again, for technical purposes, it is convenient to consider the calorific value of 1 litre—that is, in the case of hydrogen, 3·06 Calories per litre.

So far, it is clear we have gramme molecular weight or volume, according as it may be more convenient to consider the standard mass for solids, liquids, or gases, for scientific purposes, and 1 gramme or 1 litre (under specific conditions of temperature and pressure); but now we come to our national system of weights and measures.

There is a perfectly rational pound, Fahrenheit British Thermal Unit (B.Th.U.), the amount of heat required to raise 1 lb. of water 1° F. Its absolute value relative to the calorie is—

$$\frac{\text{Mass of 1 lb.} \times {}^\circ\text{F.}}{\text{Mass of 1 kilo.} \times {}^\circ\text{C.}} = \frac{\cdot 45359}{1} \times \frac{5}{9} = \cdot 2520,$$

$$\text{or 1 calorie} = 3{\cdot}968 \text{ British Thermal Units.}$$

British thermal units *per pound* are clearly expressed by a number relative to gramme calories *per gramme*, bearing the same ratio as the relative magnitude of the degree Centigrade to that of Fahrenheit—*i.e.*, 1·8 : 1.

E.g., the heat of combustion of carbon in gramme calories per gramme is 8,080; in B.Th.U. per lb. it is 14,544 (= 8,080 × 1·8).

In this country it is customary to measure gases by the cubic foot, so we have the calorific power of gas expressed as British thermal units per cubic foot (usually measured moist at 30″ barometer and 60° F.), and the Metropolitan Gas Referees have introduced the mixed value calories per cubic foot.

This somewhat inconsistent mode of expression is convenient when Centigrade thermometers and metric weights or measuring vessels are used. It is definite, and that is the main point.

Factors useful for conversion from one mode of expression to another are given in the Appendix.

CHAPTER VI.

THE CALORIMETER AND ITS SURROUNDINGS.

I. The Calorimeter Proper—Calorimetric Substances—Calorimeter Vessels; Materials, Form, Support and Locus, Size—Special Construction for Combustion Calorimeter—Mixing Devices: Stirrers; Horse-shoe or Crescent, Helical, Propeller, Motive Power. **II. Thermometers**—(1) Mercurial Thermometer—Fineness of Graduation, Limits of Visual Estimation, Range of Temperature, Determination of F.I.—Boiling Point of Water—Melting Point of Ice—Verification of Intermediate Points—Certificates from National Testing Institutions—Beckmann Thermometer—Effects of Internal Pressure—External Pressure—Lag—Difference between Mercury and Hydrogen Scale—(2) Platinum Resistance Thermometer—(3) Thermo-electric Thermometer. **III. Influence of Surroundings**—Adiabatic Calorimetry—Newton's Law of Cooling—Stefan's Law—Lagging *versus* Free Radiation—The Regnault-Pfaundler Formula—The *Locus in quo* of Calorimetric Experiments. **IV. The Capacity for Heat of the Calorimetric System**—Determination by (1) Calculation, (2) Communicating a known Amount of Heat to System, (*a*) Combustion Method, (*b*) Electrical Method—Relative Merits of these.

I. The Calorimeter Proper.

Calorimetric Substances.—For the thermometric method of calorimetry which is usually adopted, water is almost universally used as the calorimetric substance. The fact of its specific heat being taken as unity renders it particularly convenient as saving calculation and avoiding the use of intermediate substances, of which the heat capacity may be doubtful. The relatively small variation of the specific heat of water, and, above all, the ease with which it can be obtained in unlimited quantity in a very high state of purity furnish further reasons for its adoption.

It must not be thought, however, that water is the only substance which is, or has been, used as the calorimetric or receptive substance. Favre and Silbermann used a calorimeter in which mercury acted both as the receptive substance and thermometer. That is, the expansion of a large volume of mercury, when heated by the action which it was desired to measure, was utilised instead of having an independent thermometer. Much more recently Raupp has used a copper block for a gas calorimeter, and Nernst has used a similar appliance for the determination of specific heats. Féry has also used a calorimetric bomb directly as a calorimeter without immersing it in water.

It will be seen that the relatively high volatility of water causes it to be an unsuitable liquid for use at high temperatures, and in any case introduces a source of error at any temperature, which can, nevertheless, be included in a suitable correction, if experiments are conducted under reasonable conditions. Copper is in many respects an ideal substance. It is non-volatile at any temperature which would be used for calorimetry. Its conductivity for heat is very high—about 720 times that of water. Consequently, the time occupied in reaching a uniform temperature throughout a copper block is very short. For equal volumes its capacity for heat is about 0·81 that of water. When once a copper block, which it must be admitted would be expensive, has been examined and its heat capacity determined, it will need no further examination or weighing, but the calorimeter will have an invariable capacity for heat.

We do not think that any *liquids* other than water possess, on the whole, any real advantage over that substance. We shall not, therefore, trouble to consider them, but will at once discuss the general arrangement of a water calorimeter.

Calorimeter Vessels.—The first requirement for a water calorimeter is a vessel to hold the water to be used. The form and material of this vessel are of importance. If water only is to be used in it a very wide range of *materials* is presented. When reactions involving the use of acids or alkalies are to be carried out in the vessel itself certain metals are obviously unsuitable. For fuel purposes this is seldom the case. We have, therefore, a wide choice of materials. The materials in Table XIX. have been used for parts of calorimeters.

Of these, the low specific heat of platinum recommends it, because it enables us to reduce the portion of the heat value of the calorimetric system, which is not due to water, but its price places it out of the reach of most workers. Silver has few special advantages. Copper and brass are cheap, easily worked, and have well-defined specific heats.

The specific heat of copper more particularly, thanks to Nernst and his colleagues, and to Schimpf, is now well known at temperatures such as are attained in calorimetry. The older values, giving a range of from 100° to 0°, or 100° to 20° or thereabouts, are too high for calculating the heat capacity of the vessel at, say, 15°, near which temperature it will be used in most cases, since the specific heat of most bodies increases with a rise of temperature. If the capacity of the vessel is large relative to its weight the effect on an experiment is much reduced by the fact that the vessel represents only a very small fraction of the total system to be heated.

TABLE XIX.

Material.	Specific Heat.	Between	Observers.
Platinum,	0·032	18-100	Behn, Bartoli and Stracciati, Bunsen.
Silver,	0·056	0-100	Bunsen, Bartoli and Stracciati.
Copper,	0·09155	2·4-21·6	Nernst, Koref, Lindemann.
	0·0910	0	Nernst.
	0·094	18-100	Schmitz, Behn, Trowbridge.
	0·0928	50	Schimpf.
Brass (60 % copper, 40 % zinc).	0·0917	20-100	Voigt.
Ni, 24·1 C, 0·359 Mn, 0·410 } Nickel iron,	0·1180	20-100	Hill.
Lead,	0·0297	0	Schimpf.
	0·0308	50	,,
Nickel,	0·1032	0	,,
	0·1089	50	,,
Glass,	0·117-0·2182	..	Meyer.

Copper and brass vessels are very largely used for all classes of work. Glass has little to recommend it, its specific heat is not well defined, its conductivity and the radiation from its surface are uncertain. Besides, owing to its fragility, a vessel which has been carefully examined may easily be shattered, and much valuable work lost. There is no need for its use in fuel calorimetry, although it must be used for some other kinds of thermochemical work. If water only is used in the calorimeter, a copper or brass vessel nickelled or gilt and polished on the outside is perfectly satisfactory. The high conductivity of copper for heat is a great point in its favour, as we shall see later.

Form of Calorimeter Vessel.—The most convenient *form* for a metal calorimeter vessel is that of a tallish cylinder. This shape has the following advantages :—(1) It is easily constructed; (2) the surface of liquid exposed is relatively small, and hence the evaporation from the surface is also small; (3) it can easily be placed in such surroundings that the radiation from its surface shall be very small and regular; and (4) the water contained in it can easily be thoroughly mixed.

The *exterior surface* of the vessel should be highly polished, since such surfaces radiate less heat than those that are less smooth, and radiate it more regularly. They also reflect the greater part of the heat radiated to them from their surroundings. In Table XX. the emissive powers of a few polished metallic surfaces are given, although values for temperatures such as are used in calorimetry are not available.

TABLE XX.—EMISSIVE POWERS (*Hagen* and *Rubens*, *T.A.I.*, 1911. For Wave Length $\lambda = 6{\cdot}65\ \mu$ (arbitrary units).

Temperature.	Silver.	Gold.	Platinum.	Nickel.	Brass.
100°, .	. .	. .	4·45	4·65	3·56
200°, .	1·43	1·87	5·06	5·78	3·45

Support and Locus of Calorimeter Vessel.—It is necessary that the advantage of restricted radiation and absorption secured by the use of polished surfaces should not be lost by either conduction of heat from the system, convection, or horizontal currents of air, and that, as far as may be, the influence of outside bodies shall be overcome. It is, therefore, desirable to place the calorimeter on insulating *supports*, and to surround it with some *protective jacket*. For the former purpose there is nothing much better than small blocks, or a triangle, of hard wood or ebonite.

The following Table XXI., showing the conductivity in absolute units of a few substances, will act as a guide in such matters.

The question of the protective jacket may well be left for further consideration. It is sufficient now to say that the vessel must be within such a jacket.

TABLE XXI.—THERMAL CONDUCTIVITY OF VARIOUS SUBSTANCES.

Substance.	Conductivity (Calories per sq. cm. of surface conducted by a plate 1 cm. thick for a temperature difference of 1° C. in a second).
Copper, . . .	0·8915 (at 18°, Jaeger and Diesselhorst).
Brass, . . .	0·268 (at 17°, Lees).
Iron (1% C, 2% Si, ·1% Mn), . .	0·1436 (at 18°, Jaeger and Diesselhorst).
Wood (pine), . .	$0\cdot0_330$ (Forbes).
,, (radial). . .	$0\cdot0_488$ (Forbes).
Cork, . . .	$0\cdot0_3717$ (Hersch, Leaeb and Dunn).
Ebonite, . . .	$0\cdot0_337$ (Forbes).
Horn, . . .	$0\cdot0_4870$ (Forbes).
Felt, . .	$0\cdot0_4870$ (Forbes).
Water, . . .	$0\cdot0_2124$ (Chree).

The Size of Calorimetric Vessels is a matter worthy of some consideration. As platinum is now seldom used, this point can be considered from a practical point of view, independently of the question of cost. Obviously, the larger the vessel and the greater the amount of water it holds the lower will be the rise of temperature for a given mass of reacting material. This, at first sight, makes it appear that, to obtain results of high accuracy, small calorimeters are desirable. The question is not, however, so simple. The greater the rise of temperature the greater and less easy to be estimated are the losses by radiation, evaporation, and convection, and the greater the variation of the specific heat of water. Further, the radiating surface is greater proportionally in small calorimeters than large, since the area of external surface exposed by vessels of similar shape, but different sizes, is proportional to the $\frac{2}{3}$ power of the capacity. The ratios of area to capacity are shown in the following series :—

Capacity,	1	2	3	4	5	6	7	8	. .	1,000
$\frac{\text{Area}}{\text{Capacity}}$,	1	·79	·69	·60	·58	·55	·52	·50	. .	·10

The need for very sensitive thermometers is increased as size increases, unless greater quantities of reacting material are used. This may sometimes be practicable.. It will be seen, however, that the advantages of increased size rapidly fall off, and are more than compensated for by other results of increase.

A very frequently adopted size for calorimeter vessels is one holding from 2 to 2½ kilos. of water. It is seldom that this size is exceeded, but recently some very exact determinations of specific heat have been made by A. Magnus, using a calorimeter of 60 litres capacity, and Regnault used a very large calorimeter in determining the specific heat of water. Magnus' thermopile (100 copper-constantan couples) was sensitive to $\frac{1}{50{,}000}$° C. It is obvious that, for ordinary technical purposes, so large a calorimeter would be highly inconvenient, as would be such exact measurements of temperature. The vessel should be as thin as is consistent with rigidity, in order to reduce the amount of metal relative to that of water, since the specific heat of the latter is so much better known than that of any metal.

Special Construction for Combustion Calorimeters.—Calorimeters for combustion work are different from those used for many other purposes, in so far as the combustion must take place in a chamber which is separated from the water in the calorimeter, and yet is so surrounded by it that the escape of heat may be either negligible or amenable to fairly exact correction. When, as is most often the case, the products of combustion are allowed to escape, they must be cooled to a temperature closely approximating to that of the room or of the calorimeter water, as the case may be; also, oxygen for the combustion must be supplied to the fuel either as the pure gas or as air passing through the instrument, or in a substance which will easily give off oxygen.

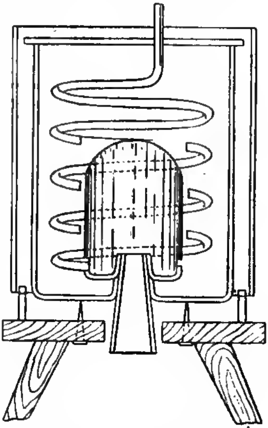

Fig. 31.—Thomsen's combustion calorimeter.

A typical arrangement for this purpose is that adopted by Julius Thomsen for combustible gases, and shown in Fig. 31.

The gas is burnt from a special burner fed with oxygen, which is pushed up the constricted neck, shown in the lower part of the calorimeter vessel, into the dome-shaped combustion chamber;

the products of combustion pass out through the spiral tube and escape at the top. In their long passage through the tube they are cooled by the water in the calorimeter vessel.

A very different instrument was used by Thomas Andrews, of Belfast.* He conducted his combustions, which were, in fact, explosions, in a thin copper vessel (Fig. 32) of 380 c.c. capacity. This was fitted with a screw plug with a cork in it, through which passed a silver wire (*a*). Another silver wire (*b*) was soldered to the screw plug itself. The wire *a* was connected to a copper band surrounding, but insulated from, the copper explosion vessel. The vessel was filled with the mixture of combustible gas and oxygen which was to be exploded. When the vessel was properly closed a spark could be passed within the mixture between the wires *a* and *b*, and the whole having been previously immersed in a vessel of water of known temperature and heat capacity, the heat produced by the explosion could be measured by the rise of temperature of the system. The thermal

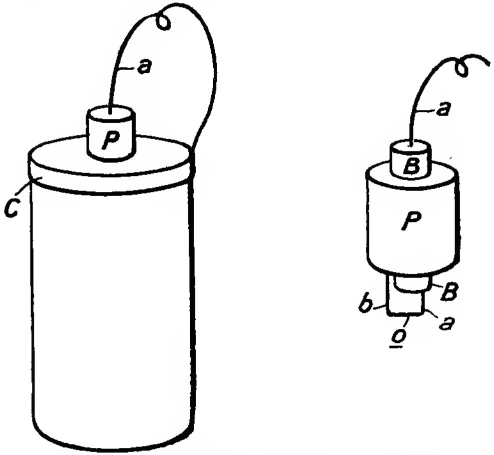

Fig. 32.—Andrews' copper explosion vessel.

a, Silver wire through cork B.
b, Silver wire soldered to screw plug P.
o, Firing wire.
c, Copper band surrounding, but insulated from copper vessel.

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* *Phil. Mag.*, vol. ccxii., p. 322, 1848.

capacity of Andrews' vessel was very low, equal to only 27·70 grammes of water.

In this apparatus we see the germ of the calorimetric bomb, afterwards associated with the name of Marcelin Berthelot. This, in its earliest form for use with gases, is shown in Fig. 33. A stout forged steel vessel *A*, lined with platinum *a*, *a*, had a well-fitting ground-in cover *B*, which was held down by a screw collar *C*. The cover, which was also lined with platinum, had a central collar with a screw thread on the inside, through which passed a tapped tubular plug *G*. At the bottom *E* the tube ended in a solid conical plug, a hole drilled in the side serving to continue the tube into a chamber with a conical seating, on to which the conical end plug could be tightly screwed by means of the milled head *F*. The bomb could thus be filled with gas and closed gas-tight or evacuated and similarly closed by turning the milled head until the conical valve was "well home." An ivory plug *I* passed through the side of the cover and carried a bent platinum wire *H*, which it also insulated from the bomb itself. A spark could thus be passed between the bent inner end of *H* and the bomb cover, if their outer parts were connected with an induction coil or other sparking apparatus. The bomb could be filled with a gas to be burnt, by exhaustion and admission of the gas through the valve *G*, either by one exhaustion and admission, or, if the pump was not very good, by a further exhaustion and admission. The vessel was meanwhile immersed in water, and the temperature and barometric pressure noted, it being necessary to fill under a slightly greater pressure than that of the atmosphere and momentarily to release the valve *G*. Oxygen under pressure was then admitted, the valve again screwed down, the bomb placed in a suitable calorimeter vessel, and, after the temperature had been properly determined, a spark passed; the heat produced by the combustion was then measured. Or, in some cases, an analysed mixture of gas and oxygen was filled into the bomb and burned.

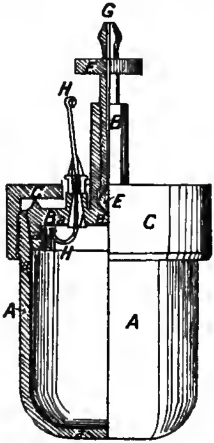

Fig. 33.—Berthelot's calorimetric bomb.

These are the fundamental types of all combustion calorimeters.

Mixing Devices—*Stirrers.*—The next point which needs discussion is the proper *mixing* of the water in such calorimeters as are not constructed for use with flowing water. In these the water is either made to pass through so narrow an aperture that its temperature at the point of measurement cannot well vary, or it flows around suitable baffle plates, and is thereby mixed. In most other cases the action, the thermal effect of which is to be measured, will probably not take place homogeneously throughout the water; in fact, it is obvious that a process of combustion must be localised in a vessel within the water, and that there will be in the apparatus a very steep temperature gradient from somewhere in the region of 1,000° to somewhere distinctly below 100°.

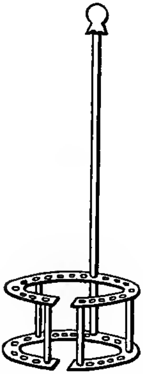

Fig. 34.—Horse-shoe or crescent stirrer.

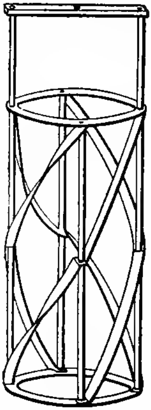

Fig. 35.—Helical stirrer.

The very low conductivity of water (see Table XXI.) renders necessary some efficient stirring process.

The *Horse-shoe or Crescent* pattern of stirrer is one of the oldest and most frequently used. It consists of one or more metal plates of the shape indicated by its name (Fig. 34), which are fixed on a vertical rod or rods in such a manner that they can be worked up and down in the water either by hand or by mechanical appliances. The plates are usually perforated either with round holes or, better, by stamping out and turning up small tongues of metal in such a manner that many small and opposing currents of water are formed. When stirrers of this kind are composed of two or more plates, the vertical movement allowed should not be so great as to permit the upper plate ever to leave the water, as loss by evaporation or splashing might occur in appreciable amount. The loss due to the repeated withdrawal of the rod or rods belonging to the stirrer is very small. If stirrers of this kind are constructed so as to fill a large part of the area of cross-section of the calorimeter vessel, and are worked at a suitable rate, say 60 to 100 strokes per minute, they are quite efficient. They possess the merit of simplicity.

Helical Stirrers (Fig. 35), consisting of curved metal plates assembled in such a manner that they impart a rotary motion to the water when they are turned, were preferred by Berthelot. They have been used by many workers, and are efficient, although in our opinion not more so than the up-and-down pattern. Although usually rotated, and built on circular frames, some patterns are only allowed to rotate through part of a circle and back again. In such forms the helical plates are assembled on roughly semi-circular frames, and the thermometer is placed in a position which is never occupied by the stirrers. Ostwald says of this stirrer that "it is at least more difficult to make and therefore dearer."

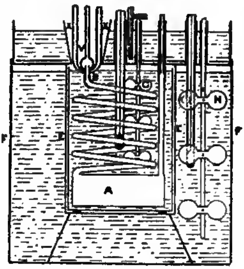

Fig. 36.—Propeller stirrer.

A "*Propeller*" *Stirrer* (Fig. 36) has been used by Th. W. Richards. A rapidly rotating copper propeller, such as would be used on a motor-boat, is placed towards the side of the vessel, and maintains a brisk circulation of water. Similar stirrers are used in the thermometer-testing baths at the National Physical Laboratory. Whichever form of stirrer is used, it should be connected with the driving motor, if one is employed, by means of a sleeve or beam of a non-conducting material, such as wood or ebonite, in order that heat exchanges, due to conduction between the system and its surroundings, may not be appreciable. It is desirable that the stirrer should be made of the same material as the calorimeter vessel, if it is proposed to determine the heat capacity of the system by means of the known specific heats and weights of its components.

Motive Power for Stirrers may be obtained by the use of either electric or water motors or clockwork. A small electric motor, such as is used to drive a ventilating fan, is sufficient for the purpose, as is a very small turbine, if high pressure water is available.

Stirring by hand, although good enough for many purposes, is likely to be irregular, and is very tiring. We do not think that the most accurate work can be done when one worker has to read the thermometer as well as to stir. When the services of a second worker are available this objection is removed, particularly if a pendulum or metronome is used to synchronise the rate of stirring.

II. Thermometers.

The Thermometer is, of course, one of the most important parts of the calorimeter, since on its accuracy depends the value of the work done. It is usually found desirable to restrict the rise of temperature, which is to occur during an experiment, according to the method used. In calorimeters of the *still-water type*—that is, those in which the water in a vessel is heated, in contact with the supernatant air, by the combustion of a more or less predetermined mass of the material to be examined, it is desirable to allow a rise of temperature not exceeding 3°, or at the most 4°. For the most exact work 2° is seldom exceeded. With greater rises of temperature the errors due to evaporation of water, radiation, and convection, and the variation of the specific heat of water are less clearly defined, and the value of any corrections greatly reduced. When, as in the case of *flow calorimeters*, a continuous stream of water in a closed system is heated by a continuous supply of gas, the rise of temperature may be greater; in fact, as much as 20° is allowed in the official working of the Boys' calorimeter, but in our opinion it is undesirable to work with so great a difference without adopting special precautions. It is, however, clear that thermometers of different degrees of accuracy are required for these various kinds of work. An accuracy of measurement of, say, $\frac{1}{200}$ of the observed rise of temperature should be aimed at in technical work, and at the worst $\frac{1}{1000}$ for research.

We may now further consider the three different types of thermometers which are practicable for use in calorimetry :—

1. The mercurial thermometer. (This is most often used.)
2. The platinum resistance thermometer. (This is very exact, and can be made to give very rapid indications, but is

less convenient than either a mercurial or a thermo-electric instrument, since an experiment and not a mere observation is required.)

3. The thermo-electric thermometer.

1. **The mercurial thermometer,** for technical work, is, at present, the most convenient, and we may usefully consider some details connected with it.

Fineness of Graduation.—For almost any calorimetric work thermometers must be graduated on a fairly open scale to $\frac{1}{10}°$ at least. Some authorities consider that there is no advantage in carrying the subdivision of the degree further than this, since it is very easy to estimate hundredths of a degree on such a scale, and with practice it is claimed by some that thousandths can be estimated with greater accuracy than in a thermometer more finely divided, but in which the thickness of the dividing lines causes appreciable error in estimation.

Limits of Visual Estimation.—We have experimented with many observers, both experienced and utterly inexperienced, and we find that it is seldom that an error of ·1 is made by any in estimating fractions of 1 cm. on cards ruled with two parallel lines 1 cm. apart and thick ink lines of varying length at right angles to the pencil lines—an arrangement very like that of a thermometer scale. Several observers evidently felt that a second decimal place was at times necessary to express their sense of relative magnitude, and in such cases the error was usually small. Whether the same sensitiveness would be shown when the divisions were only 1 mm. apart is open to question, although it must be remembered that in reading thermometers magnification would be used.

Mr. Shepherd Dawson, of Glasgow University, has kindly considered this matter from the point of view of the practical psychologist. He informs us that, having regard to the fact that Helmholtz and others have found that the limit of delicacy of local discrimination in the retina is about 1′ of an angular degree, the possibility of subdividing divisions further than into tenths is precluded when the division marks are nearer one another than would correspond to 1 mm. at a distance of 20 cm. This represents the same angular interval as would be obtained when observing the same division through a telescope of magnification 5 linear at a distance of 1 metre.

Mr. W. Shackleton, whom we have also consulted, informs us that Herschel's work on the same subject of limits of local discrimination, which he has personally repeated with similar results, tends to very similar conclusions as to discrimination of two objects, although one object of 30″ can be distinguished by some observers if it is very different in colour from its surroundings—such observation, he remarks, is rather of a photometric than a discriminative character. It must also be remembered that, although the expression "magnitude" is used of the fixed stars, it is only to express brightness, since no star has an appreciable angular magnitude, even in a telescope. He also informs us that the limit of 1′ does not hold good for the discrimination of double stars, since *very few* people can distinguish ϵ_1 and ϵ_2, Lyræ, which are 3′ 27″ apart, and such double stars as *ο Cygni* (5′ 30″), and Capricornis (6′ 13″) present some difficulty, although most people can see *ζ Ursæ Majoris* (Mizar) as distinct from its neighbour (11′ 30″).

Mr. Shackleton, however, informs us that he finds in certain cases where the temperature is not varying, he and other observers agree well in estimating to hundredths fairly wide divisions on thermometers.

The range of temperature which should be covered will vary with the nature of the work attempted, but, speaking generally, the working range for still-water calorimeters is from about 10° to 25° C., and for flow calorimeters from 10° to 45° C. As, however, it is desirable to have certain fixed points, which can be verified independently on the scale, it is better that the actual range should be greater than the above working range. It is useful for all thermometers to include the fundamental interval from 0° to 100°, but as this would result in an inconvenient length for delicate instruments, it is not usual to graduate sensitive thermometers which include this interval over the whole length; a widening of the tube is made over the highest working point, of such a capacity as to include the range from that point to, say, 98°, and the graduations are continued from 98° to 102°, or thereabouts. Fortunately, at least one other point exists which is almost as well known as those marking the extremes of the fundamental interval. This is the transition point of sodium sulphate from

$$\mathrm{Na_2SO_4, 10H_2O \text{ to } Na_2SO_4 + 10H_2O.}$$

It has been found by Richards and Wells to be

$$32{\cdot}383 \pm 0{\cdot}001 \text{ (hydrogen scale) } (= 32{\cdot}484 \text{ mercury scale}),$$

so that for still-water calorimeters a thermometer showing 0° and 33° with, say, 2° beyond each way—*i.e.*, $-2°$ to 35°—is amply sufficient.

It will be well, before further considering the various patterns of thermometers, and the means of verifying their accuracy throughout the scale, to describe methods of determining the points of the fundamental interval, the boiling point of water, and the melting point of ice.

The Boiling Point of Water is always determined first when it is wished to ascertain the value on a thermometer of the fundamental interval, for reasons which are given later. The actual determination is that of the *condensation point of the saturated vapour*, when its pressure is equal to that of the atmosphere, or the equilibrium temperature of water and steam at a pressure of 760 mm. The *boiling point of water* is subject to some variation, not only on account of any substances which may be dissolved in it, but by reason of its tendency to superheat. The Earl of Berkeley and M. P. Applebey * have investigated this point, and find that the rate of boiling, and the height of the column of water through which the steam has to pass affect it to an appreciable extent. They give a formula for calculating the variation due to these causes.

The vapour point, which is always used in thermometry, is easily determined, and is not dependent on the purity of the water boiled or on the rate of boiling, provided it is sufficiently rapid. Water is boiled briskly in a vessel with a sufficiently long and fairly wide neck. The thermometer to be tested is placed so that the whole of the stem, up to the 100° mark, as well as the bulb, may be in the column of vapour, and boiling is continued until the mercury has assumed a steady position. The reading on the scale and the height of the barometer are now taken. The temperature read will be that of the true boiling point or vapour point (t) corresponding to the barometric pressure

$$t = 100 + (h - 760) \cdot 038,$$

where h is the height of the barometer in mm., and ·038 is the variation of boiling point for 1 mm.—*e.g.*, a certain thermometer when examined gave a reading of 100·02° for the boiling point of water at 764·5 mm. Now, this temperature actually is

$$100 + (764\cdot 5 - 760) \cdot 038 = 100\cdot 17^{\circ},$$

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* *Proc. Roy. Soc.*, 1911, A. 85, p. 477.

and, assuming the graduations to be approximately equal, the true 100° point is 100·02 − ·17 = 99·85° of the thermometer.

A diagram is shown in Figs. 37 and 37*a* of hypsometers; specially protected devices for determining this point. That shown in Fig. 37 can be used in either a horizontal or vertical position. Provided the column of vapour is protected from draughts, all that is necessary is (1) that the whole column of mercury and the bulb shall be in the vapour, (2) that water shall be dripping from the bulb (it is a good plan to wrap a shred of cotton wool round it), (3) that steam is issuing freely from the instrument, and (4) that the mercury shall not be read until the column is stationary. If these precautions are observed, the temperature will be that of the true boiling point of water at the pressure indicated by the barometer. The heating of the bulb for the time required gives rise to an expansion of the glass as well as of the mercury. There is a considerable lag in the contraction of glass, hence when the whole thermometer has been cooled to zero after having been heated a temporary depression of the zero point will be noted, due to the enlarged bulb holding more mercury and the stem consequently less, although actually the capacity of the capillary is still excessive. The effect on the bulb is about 60 times that on the stem. For this reason it is necessary that to

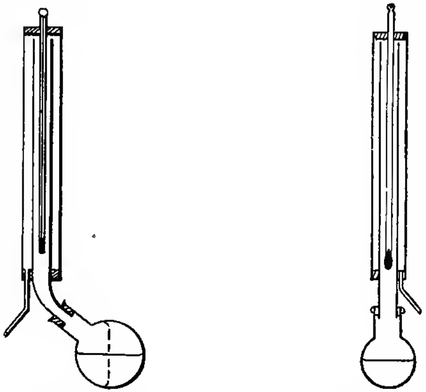

Fig. 37. Fig. 37*a*.

Apparatus for determination of boiling point of water.

determine the F.I. the boiling point determination must quickly be followed by that of

The Melting Point of Ice.—The thermometer is plunged as soon as reasonably cool into a mixture of pure ice and pure water, which is well stirred, and which reaches as high as the zero point of the instrument. The thermometer referred to above when thus treated gave a reading of 0·00. The F.I. on this instrument, therefore, equals 99·85 – 0·00, 99·85° of the scale, and the value of the scale degree is $\frac{100}{99 \cdot 85}$, or 1·0015° C.

Note.—This value holds good when the instrument recovers its normal cold-state zero unless the graduations are grossly unequal around one or other or both of the fundamental points, which is most unlikely.* The points, however, correspond to a higher place on the scale.

The practical determination of the ice point can be made as follows:—A quantity of distilled water sufficient to cover well the bulb and stem of the thermometer to the zero point is placed in a large test tube with wire stirrer. This is then put in a mixture of ice and salt until a good film of ice has formed inside the tube; next it is put inside another slightly larger tube in a beaker, bottle, or Dewar flask (Fig. 38) containing ordinary ice and water. By this means the inner tube will contain the system, ice-water, at a fixed temperature of 0° C. for a considerable time. The thermometer is then introduced, and the stirrer worked until the mercury has assumed a stationary position. This represents the true zero.

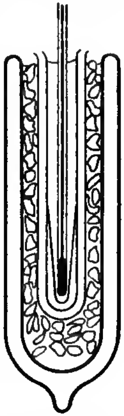

Fig. 38.
Apparatus for ice-point determination.

It is better to work in this manner rather than to use ordinary ice direct, as the ice point is affected by dissolved solids in the water, and it is impossible to be sure of the purity of ice which one has not frozen oneself from distilled water. The ice point is not absolutely unaffected by variation of pressure, but the effect of any possible barometric variation is infinitesimal. The only sources of error are impurity of the ice and local differences of temperature due to inefficient stirring.

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[*] In the particular case the calibration error nowhere exceeded 0·11°.

The Transition Point of Sodium Sulphate.—This point, which has been most carefully investigated by Th. W. Richards and Churchill, has been found by them to be extremely well defined when determined with the proper precautions. They recommend that the melting, rather than the setting, point should be taken.

Verification of Intermediate Points.—The determination of the fundamental interval, or of other fixed points, is not sufficient for establishing the value of the scale divisions throughout the whole range of a thermometer. It is necessary either to calibrate the instrument by determining the length in degrees of a detached thread throughout the whole of the scale, a method which is very tedious and requires some skill, or to compare its indications at definite intervals with those of a standard instrument. Work of this kind cannot usually be undertaken conveniently by private individuals, and it is better to obtain certificates of verification and comparison with standards from such institutions as the National Physical Laboratory at Teddington or the Physikalische-Technische Reichsanstalt at Charlottenburg. Both institutions will examine thermometers under such conditions as may be indicated as approximating to those of actual working, at as many points as may be desired, to such degree of accuracy as may be justified by the fineness of the divisions. Provided that the work is carried out, as we know it is at the former institution, and believe it is at the latter, with due care, this method seems to have some advantages over calibration, as certain errors are included in the total error noted at each point of comparison, and it is not necessary to make separate corrections for them. We give a few specimen certificates, which show the scope of the tests made.

Certificates from National Testing Institutions.—It appears to us to be an unsatisfactory plan to use unexamined thermometers, however good the makers may be, and we strongly advise that certified instruments should be used when the worker does not care to calibrate his own thermometers. The charges made for examination of the kind indicated below are small, when the really great amount of care bestowed on the work is considered, and the standards and appliances available at such institutions as those mentioned are altogether out of the reach of private individuals. We have seen the testing arrangements at Teddington, and can personally testify to the very thorough work done there.

We give, as examples, (1) a translation of a Reichsanstalt certificate for a calorimeter thermometer of the German inclosed pattern; (2) a National Physical Laboratory certificate for an English thermometer, divided stem, from 10° to 25·2° in $\frac{1}{50}$°; (3) a Reichsanstalt certificate for a 4° Beckmann thermometer divided in $\frac{1}{100}$°.

"(1) Certification of verification for the thermometer P.T.R. 45,103. The thermometer divided in hundredths of a degree C. is, as a laboratory thermometer, tested and verified; its results are at the present time--

"TABLE XXII.

14°,	0·02	degrees too high.	20°,	0·02	degrees too high.
15°,	0·02		21°,	0·02	
16°,	0·02		22°,	0·02	
17°,	0·02		23°,	0·02	
18°,	0·02		24°,	0·02	
19°,	0·02		25°,	0·01	

"The above results of testings to one-hundredth degree are based on the gas thermometer, and are obtained when the instrument up to the beginning of the scale is at the temperature to be measured, and the remainder of the mercury thread is at a mean temperature of 18°.

"As a means of identification the official number, P.T.R.,* the imperial eagle, and the number of the year are etched on the thermometer.

"Datum marks will be found at 14·005 and 25·005 degrees, etc."

In this instrument the scale begins 22 cm. above the end of the bulb, so that it would have to be immersed deeply in order to be used under the conditions of testing. The error caused by any ordinary variation of temperature, from 18°, of the emergent column of mercury would be small; the error on the differential readings generally used in calorimetry would be extremely small. The length of the scale from 14° to 25° is 32 cm., so that the mean length of a degree is 2·9 cm.

The marks made on the outer casing at 14·005° and 25·005° serve to prove at any time whether the inner milk glass slip bearing the graduations has shifted its position, although the method of mounting renders this very unlikely.

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* = *Physikalisch-Technische Reichsanstalt.*

"(2) Corrections (to the nearest 0·005° C.) to be applied to the readings determined by comparison with the standard instruments of the National Physical Laboratory.

"TABLE XXIII.

Reading.	Correction.	Reading.	Correction.
12°, . . .	− 0·045°	17°, . . .	− 0·045°
13°, . .	− 0·040°	18°, .	− 0·055°
14°, . .	− 0·045°	19°, . . .	− 0·06°
15°, .	− 0·040°	20°,	− 0·050°
16°, . .	− 0·035°	21°, .	− 0·045°

"*Note I.*—When the sign of the correction is +, the quantity noted is to be added to the reading of the instrument, and when −, to be subtracted from it.

"*Note II.*—The corrections refer to the hydrogen scale, and were obtained with the instrument immersed to the 10° point, and in a vertical position."

This thermometer was divided into $\frac{1}{50}$°, and the scale was from 10° to 25·2°. The degree length was 25 mm. (1″). It was desired that the points indicated only should be tested.

(3) A Beckmann thermometer was examined for one of us by the Reichsanstalt. The certificate states—

"The thermometer has a scale which reaches from −0·2 to +4·2, and the smallest divisions approximate to hundredths of a degree.

"The thermometer was tested in the vertical position at slowly rising temperatures. For each reading it was shaken by cautiously tapping to prevent the adhesion of the mercury thread to the walls of the capillary.

"The following are the results of testing:—

"TABLE XXIV.

Mercury Filling.	Interval of Measurement about.	Mean Temperature of Emergent Thread.	Degree Value of the Scale in °C.
I., ...	0-4	15°	0·997
II., ...	10-14	17°	1·002
III., ...	20-24	20°	1·006

"The calibration corrections are set out in a separate table.

"The foregoing results of testing are referred to the hydrogen thermometer, and hold good when the thermometer is only placed in the temperature bath to the commencement of the scale and the mean temperature of the emergent mercury column has the value given in column 3. For each 6° divergence, by which the mean temperature of the thread is found to be higher or lower than that given in column 3, the value of the degree recorded in column 4 should be decreased or increased by 0·001°.*

"As a token of the preceding testing the official number, P.T.R., and the year is etched on the thermometer. Datum marks will be found at the positions 0 and 4 on the scale.

"Examples for correction of observed differences of readings in degrees Centigrade are given.

"TABLE XXV.

Range of Measurement, ° C.	Reading of Thermometer.	Calibration Correction.	Differences of Corrected Readings.	Value of Degree for Range.	Corrected Temperature difference, ° C.
0-4, .	4·000	0·000	0·994	0·997	0·991
	3·007	− 0·001			
20-24, .	2·996	− 0·001	1·986	1·006	1·998
	1·008	+ 0·001			

A table of calculated values of the degree for different ranges from − 20° to − 15° to + 200° to + 205° is given for the glass (Jena 16^{III}),† of which the thermometer is made, and for specified

"TABLE XXVI.—Corrections for Degree Lengths.

	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0, . .	0	0	+1	+1	+1	+1	+1	+1	+1	+1
1, . .	+1	+1	+1	+1	+1	+1	+1	+1	+1	0
2, .	0	0	0	0	0	0	0	0	0	0
3, . .	−1	0	0	0	+1	+1	+1	+1	+1	0
4, . .	0	..	..	..	..	..	..	..	..	..

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* This correction is based on the apparent coefficient of expansion of mercury in glass, which is about $\frac{1}{6000}$.

† This glass can be recognised by the violet stripe along its length.

temperatures of the emergent columns, with the note that the actual degree values of the particular instrument differ from those given by 0·003 (observed − calculated = − 0·003).

The calibration errors for each ·1° interval are given in 0·001 in Table XXVI.

The length of the degree in this thermometer is 47 mm.

The Beckmann thermometer, which is much used in calorimetric and any other kinds of purely differential work, is usually, but not always, of the German inclosed pattern. The range of temperature is relatively small—usually 6°, but in some cases greater. The degrees in the shorter range patterns are numbered from 1 upwards, and are divided in fiftieths or hundredths. They do not necessarily represent any particular temperature, but only differences of temperature. The working range can be adjusted to begin at any desired temperature, by warming to above that temperature, and tipping some of the mercury from the upper part of the capillary into a small reservoir at the top, by tapping the bulb when the thermometer is in a vertical position, on the palm of the hand or on a blotting-pad or rubber block. By this means one thermometer can be made to serve for any experiments, such as a calorimetric determination or a depression of solidifying point, or raising of boiling point in molecular weight determinations by Raoult's or Beckmann's methods. It is clear that if such a thermometer is used for very widely differing temperatures the amount of mercury abstracted from the expanding system and the alteration of volume of the bulb will cause an alteration—an increase—in the value of the degree at the higher temperatures. This may be determined by comparison at such temperatures of the extreme points of the scale with a less finely graduated, but accurate, thermometer of the ordinary kind, when a mean value of the degree for that temperature range can be obtained. Some Beckmann thermometers, usually graduated in $\frac{1}{10}$° or $\frac{1}{20}$°, have a range of more than 20°, and when all the mercury is used in the expanding system read ordinary temperatures from, say, 0° to 20° or there-

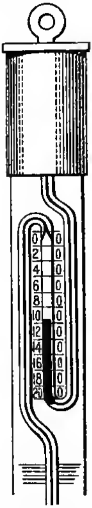

Fig. 39.—Beckmann thermometer with auxiliary scale.

abouts. Within this range, therefore, instruments of this kind can be used as ordinary thermometers, and any change of zero can be determined when desired.

A useful addition to the ordinary differential Beckmann thermometer is a scale to the upper reservoir (Fig. 39), showing when the required temperature is reached for the thread to be broken, in order to give the intended range of temperature. It must be borne in mind that it is only intended for the approximate adjustment of the instrument, and is not in any sense a thermometer scale for actual measurements.

From what has already been said, it will be seen that thermometer readings need correction for errors (1) of the F.I. (*i.e.*, the value of the degree), (2) of the zero point, (3) of calibration, and (4) those due to the portion of the mercury column emergent from the temperature to be measured. In a properly annealed ordinary thermometer which has been compared with a standard all these errors are included in the corrections given for the various points ; in a Beckmann thermometer, as the certificate (3) shows, they must be made separately. Some other sources of error must be noted. They are—

(5) Internal pressure.
(6) External pressure.
(7) Lag.
(8) Differences between mercury and hydrogen scales.

Of these, the lag is the only one which need be separately corrected for.

(5 and 6) *External and Internal Pressure.*—If the *external pressure* on a thermometer bulb varies it will obviously affect the volume of the bulb, and thus cause an error in the readings, which will be of the nature of zero or index error. The magnitude for any ordinary change of pressure, it is fairly evident, will not be great, and it will not affect the *difference* between two readings, since it is common to both. Hence, in a calorimetric experiment the depth of immersion is immaterial, in so far as it affects the rise of temperature in this way, although, of course, the exposure correction may be worth making. The varying heights of the column of mercury at different temperatures, when the thermometer is used in a vertical position, will affect the volume of the bulb, and will cause the readings in a vertical position to be lower than those taken in a horizontal position by an amount

proportional to the rise of temperature above the zero or any other fixed point. If the coefficient of internal pressure β_i of a thermometer be determined by taking the value of the fundamental interval in vertical and horizontal positions, and dividing the observed difference by the height of the degree observed above the middle of the bulb, we thus get the correction for 1 millimetre of mercury column. The correction C_{t_1} for any temperature t_1 becomes, therefore,

$$C_{t_1} = \beta_i \, l_{t_1},$$

and for any other temperature t_2

$$C_{t_2} = \beta_i' \, l_{t_2},$$

when l_t equals the height of the observed degree in mm., so that

$$C_{t_1} - C_{t_2} = \beta_i \, (t_1 - t_2) \, ;$$

that is, it is proportional to the difference of temperature *if the degree length is uniform.* This is usually the case, so that in such cases the correction is included in the value of the degree, if the fixed points for graduation are determined in the vertical position and the thermometer is used in that position. It also is included in the correction obtained by direct comparison with a standard thermometer.

If the thermometer has, as is often the case, an auxiliary expansion between, say, zero and the working range, or between the working range and 100°, the case is not so simple, since a rise of several degrees in these places will affect the internal pressure very little. Here, again, comparison with a standard eliminates the error, or it can be dealt with by a method indicated by C. Chree.* This paper (pp. 205-227 and 299-325) deals with many questions of thermometry in a practical manner, and from the point of view of the Kew authorities, Chree very pertinently remarks that, "for many purposes, including even some investigations of high scientific importance, the measurement of temperatures to 0·001° C. is just as futile as the use of 10-figure logarithms in handling data in which the fourth significant figure is uncertain." He also admits that, "on the other hand, there unquestionably exist physical and chemical investigations, tending to increase in number, in which the absolute determination

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* "Notes on Thermometry," *Phil. Mag.*, vol. xlv., p. 311, sect. 29.

of temperatures with the highest possible precision is of fundamental importance. For these, in the meantime, English glass thermometers and ordinary British methods are not suitable."

(7) *The lag of a thermometer* is literally the amount by which its indications "lag behind" the actual temperature of the medium in which it is placed. It is a matter of common experience that when a thermometer is placed in water hotter or colder than itself some time elapses before the mercury attains a stationary position. The effect of this lag, which is obviously due to slowness of conduction of heat through the glass and within the mercury itself and to friction in the capillary, is to cause the recorded temperatures of a calorimetric experiment to be somewhat lower than they should be during the heating period, and somewhat higher than they should be during the cooling period. Some undue flattening of the curve at its topmost part will also occur. An examination of this error, which we have already stated is very small, may be considered desirable.

By Newton's law of cooling a hot body surrounded by a cooler body will lose its excess of temperature at a varying rate, which, at any instant of time, is proportional to the difference of temperature between the bodies at that instant. If we indicate the difference of temperature between the bodies by $\theta_t - \theta'$, then the rate of cooling can be expressed by

$$\frac{d\,\theta}{d\,t} = (\theta_t - \theta')\,k,$$

when k is a constant—the cooling constant—dependent on the conditions of the experiment and $t =$ the interval of time.

Now, the course of all such cooling experiments can be expressed by the exponential formula

$$\theta_t - \theta' = (\theta_0 - \theta')\,\varepsilon^{-kt}.$$

The value of k is so enormous in well-constructed thermometers when θ_0 is the original temperature of the hotter body —that is, the lag is so small—that the plan adopted of taking cooling readings at equal intervals, as in calorimetric experiments, can hardly be followed. If, however, we so arrange that θ', which is the temperature of the cooler substance (water), is constant by making its mass large relative to the thermometer and adjusting the initial temperature of the thermometer θ_0, so that $\theta_t - \theta'$ may be equal to one-half the original excess of temperature over the water, we have t as a value to determine by observation, and can easily calculate k, for if $\theta_t - \theta' = \frac{\theta_0 - \theta'}{2}$, then

$$\tfrac{1}{2} = \varepsilon^{-kt} \text{ or } -\log_\epsilon \tfrac{1}{2} = k\,t,$$

that is,

$$k\,t = {\cdot}69315,$$

$$\text{or } k = \frac{{\cdot}69315}{t}.$$

In an actual experiment with a Beckmann thermometer the temperature of the water was 0·0. The thermometer was then taken out of the water, warmed in the hand, allowed to cool to 4·0°, so that the half point should be at the easily identified mark 2·0°. It was then plunged in the water. The time of cooling taken with a stop watch was 6·8 seconds. From this the value of k was found to be

$$\frac{{\cdot}69315}{6{\cdot}8} \times 60 = 6{\cdot}1.$$

This represents the rate of cooling for a difference of temperature of 1° per minute, although clearly it would not actually cool in one minute to this extent.

It may be asked, Why not take the time required to attain the same temperature as the water?

This would be impossible to determine owing to the gradual flattening of the curve and the difficulty of reading. For example, the thermometer in question would cool to

$\frac{1}{10}$ of the original difference in ·38 minute.
$\frac{1}{100}$,, ,, ·76 ,,
$\frac{1}{1{,}000}$,, ,, 1·13 ,,
$\frac{1}{10{,}000}$,, ,, 1·52 ,,

The errors of determination of these points would be much greater than that of the half point. The method of using the value k, when it has been obtained, must now be considered. Errors due to thermometric lag will be of two kinds—(*a*) those of the heating period, in which all the recorded temperatures are *lower* than the actual temperatures of the mass of the calorimeter. These errors will not affect the final temperature reading directly, but will do so indirectly, in so far as the total temperatures in the Regnault-Pfaundler formula (*vide infra*) will be too low, or if a graphical method of computation be adopted the area of the figure included under the heating curve will be too small. (*b*) The *excess* temperature of the chosen ordinate t_n, to which it is decided to apply all corrections, in order to obtain the final true rise of temperature.

Now, if during any interval,

a = apparent rate of change of temperature of the water,
k = the cooling constant of the thermometer,
θ = mean temperature of water, and
θ_1 = mean temperature of thermometer,

then

$$a = (\theta - \theta')\,k,$$

and

$$(\theta - \theta') = \frac{a}{k}.$$

The mean apparent rate of rise of temperature during the heating period = total apparent rise ÷ number of intervals. For any one interval the apparent rise divided by the constant k will give the error of mean temperature during that interval, and for all the intervals from, say, 0 to n (*cf.* p. 182, *et seq.*, correction for radiation), the total error will be

$$\sum_{(\theta-\theta')_1}^{(\theta-\theta')_n} = \frac{t_n - t_0}{k}.$$

It is irrespective of the number of intervals, since the mean rate decreases as the number of intervals increases. The value is also correct when, as is always the case, t_n is beyond the maximum temperature. It is obviously *added* as an extra term to the sum of the temperature in the R.P. formula. We now have to consider the direct effect of thermometric lag on the chosen ordinate of temperature t_n. At this point the rate of change is very small, and again

$$\theta - \theta' = \frac{a\ (v_1 \text{ of the R.P. formula})}{k}.$$

This correction is — in sign, as when cooling the observed temperatures are too high.

(*c*) A further correction, which will usually be still smaller, will affect the value of t_0. Its magnitude is—

$$\frac{v}{k} \text{ (of the R.P. formula).}$$

For a rising initial temperature it should be added to t_0, and for a falling temperature be subtracted from t_0, thereby increasing the value $t_n - t_0$.

For the Beckmann thermometer above considered, the total value of the correction for lag would be, for an experiment in which the value $t_n - t_0 = 2\cdot000°$, $v = \cdot004$, $v_1 = \cdot008$.

$$(a)\ \frac{2\cdot000}{6\cdot1} = \cdot33 = \text{total deficit of sum of ordinates.}$$

$$\frac{\cdot33\,(v_1 - v)}{2\cdot000} = +\,\cdot0007$$

$$(b)\ t_n \quad \frac{\cdot008}{6\cdot1} = -\,\cdot0013$$

$$(c)\ t_0 \quad \frac{\cdot004}{6\cdot1} \qquad \begin{array}{r} +\,\cdot0007 \\ \hline +\,\cdot0001 \end{array}$$

The total correction is about ·0001°. If v had a — value—that is, if the calorimeter were rising in temperature at the beginning of an experiment—the value of (*a*) would be

$$\frac{\cdot33 \times v_1 - v}{2\cdot000} \qquad +\,\cdot0020$$

$$\text{of } (b) \qquad \text{still} \qquad -\,\cdot0014$$

$$\text{of } (c)\ t_0 \quad \frac{-\cdot004}{6\cdot1} \qquad \begin{array}{r} -\,\cdot0007 \\ \hline -\,\cdot0001 \end{array}$$

Here again the correction is negligible.

When it is considered that the thermometer in question had a high lag or low-cooling constant, as the following figures show, it will be seen that it is not often that the error introduced hereby is of any consequence in ordinary work.

4°, Beckmann thermometer, . . .	k = 6·1
(— 6° to + 21°) 27°, Beckmann thermometer,	7·3
(+ 10° to 25°) English solid stem thermometer,	13·9
German enclosed thermometer, . .	..
(0° and + 11° to + 22° and 32°) English solid stem thermometer, . . .	9·2

A graphical method of correcting for lag has been described by Richards, Henderson, and Forbes.* For a good short discussion of the errors of thermometers as affecting calorimetry, see Huntly, *Journ. Soc. Chem. Ind.*, p. 1435, 1910.

Difference between Mercury and Hydrogen Scale.—An error which may affect the results of calorimetric work to an appreciable extent is the irregularity of the value of the degree of the mercury thermometer due to the variable expansion of mercury and the several glasses which are used by thermometer makers, and to the alteration of zero during heating. The curves (Fig. 40) show the variation of thermometers made of two kinds of Jena glass and the French glass used by Tonnelot, which is very similar in behaviour to 16^{III} for different temperatures compared

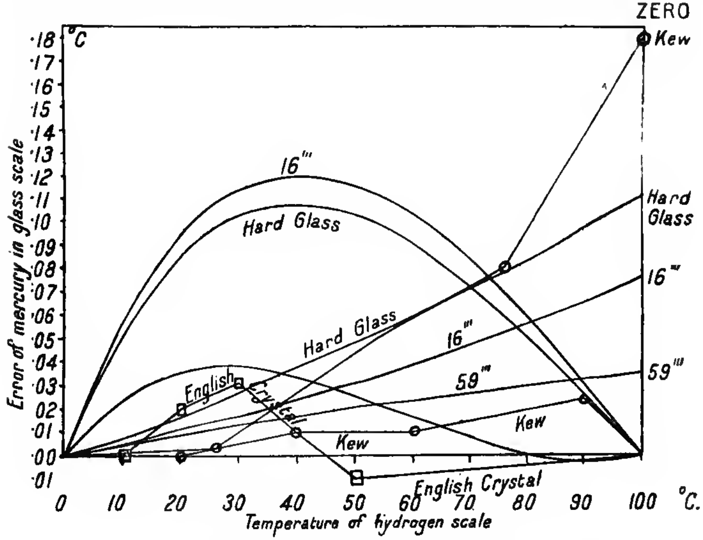

Fig. 40.—Comparison of hydrogen and mercury thermometers.

The curves showing high values at 100° indicate the error due to temporary depression of zero. (Sign of error −.)

The curves showing no error at 100° indicate the divergence from the hydrogen scale. (Sign of error + above line; − below line.)

Hard glass = Tonnelot's "verre dur."

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* *Zeit. f. Physikal Chem.*, vol. lii., p. 554, 1905.

with the hydrogen scale. For either of these glasses the 10° on the hydrogen scale between 10° and 20° C., the range within which most experiments with still water calorimeters will fall, is equal to 10·04° mercurial (the error varies between this range from 0·25 to 0·4 per cent.). For the glass 59^{III} the error is much less.

The Jena glass 59^{III} is a borosilicate glass, and may be used for temperatures up to 550° C. by those who care to use mercurial thermometers at this temperature.

2. **Platinum resistance thermometers** have been used very largely for the measurement of high temperatures, and, although not largely used for calorimetry, they have been used in very important work of this kind—*e.g.*, Callendar and Barnes' and Callendar's determinations of the specific heat of water and Fischer and Wrede's determination of the heats of combustion of several substances.

The relation of electrical resistance to temperature for platinum has been carefully investigated. The so-called platinum temperature $p\,t$ is based on the assumption that the relation between temperature and electrical resistance of platinum is linear—*i.e.*,

$$R_{pt} = R_0 (1 + a\,p\,t)\,;$$

this can be reduced to true temperature on the air thermometer scale by means of the formula

$$t - p\,t = 1{\cdot}50\,t\,(t - 100)\,10^{-4} = 1{\cdot}50\,(t^2 - 100t)\,10^{-4}.$$

The figure 1·50 is an average value of the constant, which varies but little. This value, and also the value of a, in any particular instrument can be found by determining its resistance at 0°, at 100°, and at the boiling point of sulphur, about which some small uncertainty exists. The best value is probably 444·5° C., and the divergence from this is only a small fraction of a degree (*cf.* Callendar).* The alteration of resistance between 0° and 100° will give the value of the increment of resistance per platinum-degree, and the discrepancy between the platinum-temperature for the boiling point of sulphur, calculated by extrapolation, and the correct boiling point gives the value δ, which is above represented as 1·50. Any variation from this will be due to impurity in the platinum.

Callendar's pattern of resistance thermometer (Fig. 41), in its best form, consists of a coil of pure platinum wire ·01 cm. dia-

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* *Phil. Trans.*, A. 212, 1, 1912.

meter, the "bulb," fused to thick platinum leads, about 7 cm. long. These are fused to silver leads. The object of this is partly to avoid possible contamination of the fine wire with silver, and partly to diminish conduction along the tube near the "bulb." Irregularities of resistance due to the temperature gradient along the leads are compensated by a similar pair of platinum leads connected by a short piece of fine wire such as the coil is made of, and laid parallel with the leads from the coil in a glass tube which contains the whole arrangement. The parts are insulated from one another by means of mica discs, bored with four holes and spaced at intervals of 2 cm. throughout the length of the tube by mica crosses.

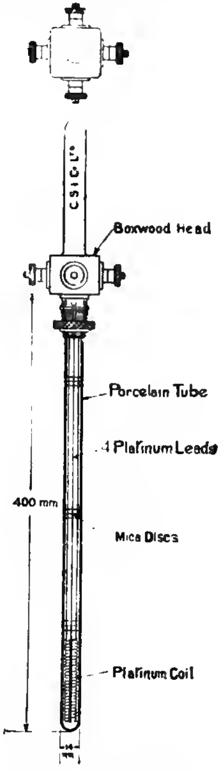

Fig. 41.—Callendar's resistance thermometer.

The resistance of the wire is determined by Callendar by means of a Wheatstone's bridge, so arranged that the resistances on both sides are approximately equal and constant. Any heating effect due to the passage of the current itself will, therefore, not vary. The compensating leads are connected on the opposite arm to the leads from the coil, and automatically correct any irregularities due to what may be regarded as exposure error. A deflectional method as a fine adjustment may be combined with the "null" approximate adjustment of the contact with the bridge wire.

We give an example from Callendar's Bakerian lecture of the calibration of a platinum thermometer.

TABLE XXVII.—Calibration of a Platinum Thermometer.

Steam at 100·262° C., .	1785·39	$p\,t_s$ deduced, . . .	422·09
Ice at 0° C., . . .	1284·07	t_s from barometer, . .	445·22
Fundamental interval.	500·03	$t_s - p\,t_s$. . . .	23·13
Sulphur reading, . .	3394·67	Difference-coefficient × 10^4,	1·505

The figures in the first four lines represent resistances. The resistance difference for 100·262° is 501·32 box units; for 100 it is

$$\frac{501 \cdot 32}{100 \cdot 262} \times 100 = 500 \cdot 03 = \text{F.I.}$$

The difference for sulphur is $3394 \cdot 67 - 1284 \cdot 07 = 2110 \cdot 60$

$$\frac{211060}{500 \cdot 03} = 422 \cdot 09° \; p\, t.$$

The boiling point of sulphur actually determined and corrected to 760 mm. [S.B.P. $= 444 \cdot 53 + \cdot 09 \;(h - 760)$] was 445·22. The difference, therefore, was 23·13. Now,

$$\begin{aligned} t - p\,t &= \delta\, t\,(t - 100) \times 10^{4}, \text{ therefore} \\ 23 \cdot 13 &= \delta\, 445 \cdot 22\; (445 \cdot 22 - 100) \times 10^{-4} \\ &= \delta\, 445 \cdot 22\; (345 \cdot 22) \times 10^{-4} \\ &= \delta\, 1 \cdot 535. \\ \delta &= 1 \cdot 505. \end{aligned}$$

The values for δ in four such thermometers which were used together were respectively 1·505, 1·506, 1·506, 1·505. This difference from 1·5000 would not affect the scale of the thermometers by so much as 0·002 at 50° C.

A defect of the Callendar pattern thermometer adduced by Jaeger and von Steinwehr is the rather high lag. These authors * describe a form of platinum thermometer (Fig. 42) which they consider particularly suitable for calorimetric work, as it has a lag so small that it cannot be measured.

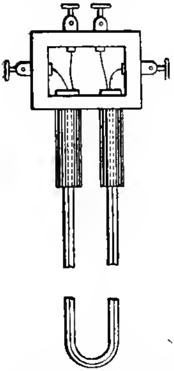

Fig. 42.—Jaeger and Steinwehr's thermometer.

The platinum wire, which is silk-covered, is ·01 square millimetre in section and 30 cm. long; its resistance is about 4·5 ohms. Its ends are soldered to the middle of copper loops which are connected with the terminals at the head of the instrument. It is inclosed in a fine metal tube (copper for choice), from which the soldered points and the wires generally are well insulated. Sulphur which was used in an earlier form, in which the wire was inclosed in a glass tube, is probably used in this metal pattern, but the description available did not make

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* *Verhand l. d. Deutsch physikal Gesellsch.*, vol. v., p. 353, 1903.

this clear. Obviously many materials are suitable. The soldered points are about 10 cm. below the level to which immersion of the instrument is recommended. The ends of the copper loops are attached to four binding screws insulated from one another on an ebonite frame.

The method of measurement of the resistance and of calculation of temperature adopted by Jaeger and Steinwehr is different from that of Callendar. They use Holborn's formula—

$$w_t = w_0 (1 + 0{\cdot}003966\, t - 0{\cdot}0_6582\, t^2),$$

where w_t and w_0 represent the resistances at t° (gas thermometer) and 0° respectively.* *Heræus* has constructed another form of resistance thermometer, in which the wire is coiled round a quartz glass rod, slid in a quartz glass tube, and the whole fused together.†

3. **The Thermo-electric Thermometer.**—Although it is not used to a great extent in calorimetric work, its convenience for many purposes and the wide range within which it can be used justify its description here. We may mention that it is used in the following commercial instruments: Féry's gas calorimeter, Junker's recording gas calorimeter, and Féry's calorimetric bomb.

As already stated (p. 128), Seebeck observed that when one of the junctions of two metals joined so as to form a closed circuit is heated an electric current flows through the metals in a direction depending on their thermo-electric properties. This effect has been carefully studied by several observers, notably Le Chatelier, who have in the case of several metals and alloys determined the quantitative relationship between the difference of temperature of the junctions and the potential difference (electromotive force) between them. The relationship does not appear to be similar for all the metals studied, and some are obviously unsuitable, from their thermo-electric properties, for accurate temperature measurements within any range; others, though unsuitable over one range, may be suitable for others.

For the temperatures which are likely to be reached in ordinary calorimetry the most suitable couples are those made with copper and an alloy of copper and nickel (Cu 60, Ni 40), known according to its origin as "constantan" or "eureka." For such couples the difference of potential over a fairly wide range is nearly pro-

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* See Ostwald-Luther, *Physiko-Chemische Messungen*, 1910.

† *Zeit. für Inst. Kunde*, vol. iv., p. 116, 1907.

portional to the difference of temperature. The actual variation of E.M.F. with temperature is expressed fairly exactly by expressions of the general form.

$$(1) \qquad E_0^t = a + b\,t + c\,t^2,$$

$$\text{or } (2) \qquad E_0^t = m\,t^n, \text{ which may be written}$$

$$\log E_0^t = n \log t + \log m,$$

when E_0^t represents the sum (in microvolts) of the electromotive force between 0° and the temperature of the cold junction, and t the temperature of the hot junction. a, b, c, n, and m are constants ascertained by experiment.

Le Chatelier * gives a formula due to Pecheux based on (1) for the E.M.F. generated in a copper-constantan couple between 0° and 250° C.

$$E_0^t = 40\,t + 0{\cdot}03\,t^2.$$

This is stated to represent the relation between E.M.F. and temperature to a fraction of a degree. It will be noted that where t is small the value of $0{\cdot}03\,t^2$ will not be great, and the E.M.F. will be roughly proportional to temperature.

For many purposes it is not necessary to measure E.M.F. directly, but rather to arrange (by a constant resistance) that the current may be proportional to the difference of potential generated in the circuit. This may be done with any sufficiently sensitive galvanometer, provided the relationship between current and deflection is known, and also provided that the resistance of the circuit is sufficient for any small variations due to changes of temperature in the conducting wires to be negligible. The usual form of galvanometer employed is a swinging coil instrument of the D'Arsonval or Ayrton-Mather type. The former is more often used, either as a mirror instrument or in the more robust pivot form. A convenient pattern of the latter (a millivolt meter) indicates either millivolts or 20 microvolts per scale division, according as one or other of two resistances is used in connection with the swinging coil. The deflections of properly constructed mirror or pivot galvanometers are practically proportional to the current passing through them—that is, in a circuit of constant resistance—to electromotive force.

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* *Measurement of High Temperatures*, p. 167.

The relatively high E.M.F. generated by a copper-constantan couple makes it very useful for general thermometric as distinguished from pyrometric purposes, for which no base metal couples are as suitable as those of platinum, platinum-iridium, or platinum-rhodium. It is often desired in the course of calorimetric or other physical work to measure differences of temperature amounting to only a few degrees, to an accuracy of, say, $\frac{1}{10}^{\circ}$. We do not refer to the principal measurements of still-water calorimetry, in which a much higher order of accuracy is necessary, but to various auxiliary measurements. For these purposes the current measuring or deflectional method is good enough. For very accurate work it is much better to use a null or zero method, and to balance the E.M.F. generated by means of a potentiometer, with a known fraction of the E.M.F. of a standard cell. This, of course, involves the use of rather elaborate apparatus, which should be carefully calibrated or standardised before use, but it is sounder in detail than the deflectional method. We do not think that for such accurate work thermo-couples offer, in most cases, any advantage in point of convenience of manipulation over well constructed platinum resistance thermometers.

In making thermo-couples, it is not sufficient to twist the ends of the wires together; they must be in absolute metallic union for satisfactory contacts to be made. We find that for small work eureka wire of 30 gauge or thereabouts twisted up for a centimetre or so with copper of the same gauge, and then the junctions either soft soldered or dipped in borax and melted at the ends in the blowpipe flame make satisfactory couples, which can be used in almost any situation where a temperature of ordinary range is to be measured, and will give a reasonable deflection with a galvanometer of fair sensitiveness. The junctions are so arranged that the leads to the galvanometer may be of copper, the constantan wire being used for the direct connection between the temperatures to be measured. Since the method is purely differential, the cold junction should be in melting ice, or in some other substance of known temperature, unless it is desired to determine differences of temperature only.

The resistance of constantan is high, that of 1 metre of wire gauge 30 is about 6 ohms. Due regard must be given to this in making couples, and it must be borne in mind that when working by a galvanometer method a variation of the resistance of the circuit will alter the relation between galvanometer readings and temperature. The copper wires, at any rate for calorimetric experiments, should be fine near the junction, so as to minimise heat losses due to conduction along the wires. At a little distance from the actual junctions thicker copper leads may be soldered to the thin wires. All connections must be very good, as the E.M.F. to be measured is in any case very small. Mercury cups are preferable to binding screws.

III. The Influence on the Calorimeter of its Surroundings.

This is a point of great importance in practical calorimetry. It is clear that, if these are not of the same temperature as the calorimetric system, the tendency of all things to come to a dead level will lead to a continual exchange of heat by radiation and absorption between them until the temperature is uniform—*i.e.*, *heat will be lost or gained by the system irrespective of the change which is the subject of experiment.* Errors of appreciable magnitude are thereby introduced.

Adiabatic Calorimetry.—Supposing that uniformity of temperature between calorimeter and surroundings is obtained at the beginning of an experiment, this uniformity cannot *easily* be sustained throughout the experiment until the final rise or fall of temperature is reached, although in fact this has recently been achieved by Richards, Henderson, and Forbes, who surround the calorimeter with a jacket, the temperature of which is altered at the same rate as that of the calorimeter itself. Fig. 36 shows an arrangement adopted by Richards and Matthews for determining the heat of evaporation of water. The vessel E.F. surrounding the calorimeter contains dilute alkali, and small portions of sulphuric acid are added from time to time to raise the temperature by its heat of neutralisation. H and C are stirrers in the jacket and calorimeter respectively.

Although such arrangement is not convenient for general use, it is clearly desirable to take steps to minimise as much as possible the effects of radiation from or absorption by the calorimetric vessel. To do this the earlier workers placed the calorimeter in a nest of badly conducting material—*e.g.*, swansdown, such as in Favre and Silbermann's calorimeter. Count Rumford adopted the ingenious plan of starting with the calorimeter as much below the temperature of the surroundings as it would be above at the finish. This involved a knowledge of the probable rise of temperature, and could only be correct when the rate of change of temperature was uniform, for reasons which will be seen later.

Newton's Law of Cooling.—It was, however, felt that expedients of this kind were not altogether satisfactory, and various attempts were made at rational correction based on Newton's well-known law of cooling. This law, which was founded on experiment, is to the effect that the rate of cooling of a heated body is proportional to the difference between its temperature and that of its surroundings; it may be expressed thus—

$$v = k(t^1 - t),$$

where v = the rate of cooling at any moment when
t = the temperature of the surroundings,
t^1 = the temperature of the heated body, and
k = a constant dependent on the conditions of the experiment.

Work which has been carried out under conditions of exactitude, impossible in Newton's day, has shown that this law is not absolutely correct, although for small ranges of temperature no sensible error is caused by using it.

Stefan's Law.—Stefan, by examination of some of Tyndall's experimental data, and Boltzmann, from thermo-dynamic grounds, found that the amount of radiation from the so-called "black bodies" conceived by Kirchoff—*i.e.*, surfaces so contrived that the emanation of heat shall be as great as if all the heat falling on them were radiated—varied as the fourth power of the absolute temperature. The sum of exchanges, therefore, between two bodies at temperatures of T and $T + t$ respectively would be proportional to $(T + t)^4 - T^4$.

These expressions equal

$$T^4 + 4T^3t + 6T^2t^2 + 4Tt^3 + t^4 \text{ and } T^4 \text{ respectively};$$

but *if t is very small relatively to* T, then certain quantities in $(T + t)^4$ may be omitted as negligibly small, so that the expression representing the amount of radiation becomes $T^4 + 4T^3t$.

$$T^4 + 4T^3t - T^4 = 4T^3t.$$

That is, the exchange is proportional to a constant quantity $4T^3$ multiplied by t, therefore within certain limits it is proportional to the value of t—*i.e.*, to the difference of temperature which is in accordance with Newton's law of cooling.

Some examples will show the range of temperature within which this assumption holds.

TABLE XXVIII.—RADIATION CALCULATED FROM THE FOURTH POWER LAW.

° C. T + *t*.	Absolute Temperature.	Heat Radiated (at 15° = 1).	Difference of Temperature, *t*.	Radiation.	Error per cent. of Newton's Law.
15, . .	288	1·0000	0	0·0000	..
16, . .	289	1·0140	1	1·000	..
17, . .	290	1·0281	2	2·007	·35
18, . .	291	1·0423	3	3·021	·70
19, . .	292	1·0567	4	4·050	1·25
20, .	293	1·0713	5	5·092	1·94

The error within the above range of 5° is small, if we assume that Newton's law is correct. Now, in calorimetric work "black body" conditions are not satisfied, and Stefan's law does not, in fact, give us a more definitely accurate expression than Newton's for such experiments. It must be borne in mind that our whole object is to be able to estimate with sufficient accuracy those heat changes which occur in a calorimetric experiment, but are not an essential part of the value, which is the subject of measurement. If, therefore, we find, on a consideration of some of the consequences of Newton's law, that it affords a convenient means of doing this, it will serve all our purposes. Since the errors due to losses or gains of this kind are not great, a relatively large percentage error in any correction for them will not affect the final result to a serious extent.

It follows from Newton's law that the loss of temperature during each of several successive equal intervals of time will be a constant fraction k, *the cooling constant* of the mean excess temperature of the interval. If the rate of change is small in each interval, then the variation of temperature during any one interval will be negligible, and the initial or any observed temperature during that interval may be taken as its mean temperature, without serious error.

If the change is more rapid, the intervals must be made smaller, or steps must be taken to estimate the mean excess temperature over surroundings of each—*e.g.*, it may be sufficient to assume that the *change* of temperature during an interval is uniform, and then the mean excess temperature of an interval between, say, the readings 0 and 1 will be equal to $\frac{t_0 - t_1}{2}$. We will, however, suppose that the changes are very small. Then for a series of intervals (initial) 0, 1, 2, 3, 4, 5 . . . n, the value of k, the cooling constant, or the loss during one interval for a difference of 1° will be $\frac{t_0 - t_1}{t_0}$, and $(1 - k)$ will represent the value of each temperature relatively to that of the preceding interval—that is,

$$\begin{aligned} t_0 &= t_0, \\ t_1 &= t_0 (1 - k), \\ t_2 &= t_1 (1 - k) = t_0 (1 - k)^2, \\ t_n &= t_0 (1 - k)^n, \end{aligned}$$

or

$$\log t_n = \log t_0 + n \log (1 - k);$$

t_0 to t_n in each case representing the excess of temperature over surroundings—that is, whereas the curve of falling temperature is a die-away curve, that of logs of falling temperature is a straight line.

If k is small and n not very large, then the value $(1 - k)^n$ may be taken as approximately $1 - n\,k$, since the other terms of the expression will be so small. Thus if $k = \cdot 01$ and $n = 10$,

$$\begin{aligned} (1 - k)^n &= \cdot 9045, \\ 1 - n\,k &= \cdot 9000, \end{aligned}$$

a difference in value of 0·5 per cent. So that *where the value of t is not changing rapidly the amount of change may be taken as proportional to time for a reasonably long interval,* and we can get a cooling rate almost uniform; sufficiently so for the purpose of correction. An inspection of the curve of temperature of a cooling experiment shows this.

The true value of $(1 - k)^n$ or of t_n can also be obtained by the exponential formula, in which $(1 - k)^n$ is expressed as a function of ε,

$$t_n = t_0 \varepsilon^{-kn}.$$

For the values $n = 20$ and $k = \frac{1}{100}$, we get by this means $t_n = t_0 \times \cdot 8187$, whereas by the previous formula $(1 - k)^n = \cdot 8181$, if 5-figure logarithms are used; but with a 7-figure table the same value is obtained—*i.e.*, ·8187.

The approximation $1 - n\,k$ gives ·80, an error of only 2 per cent.

Note.—The value of $k = \frac{1}{100}$ is higher than is usually found in good calorimetric experiments.

Lagging versus *Free Radiation*.—The fact that the heat exchanges between bodies follow Newton's simple law for small differences of temperature gives, therefore, the opportunity for a rational mode of correction, provided certain precautions are taken. This is a better plan than "lagging" the calorimeter with non-conducting materials and assuming no loss or gain to occur, or using corrections based on no fixed principles. The exchange between calorimeter and surroundings should, in the first place, be made as regular as possible. This regularity is best obtained by having the bright cylindrical vessel, in which the reaction takes place, surrounded at a distance of about $\frac{3}{4}$ inch or more by a concentric double-walled vessel holding a large quantity of water, *the larger the better*. By this means the influence of small changes of atmospheric temperature is greatly reduced and regularised, as is also that of the proximity of the person of the observer. Therefore, the variation during the initial period before starting an actual experiment is very small. Further, the inner walls—contiguous to the outer walls of the calorimeter vessel—of the water jacket are painted white with a suitable "enamel." The exchanges during the whole period of an experiment are by this means made very small, and, as the effect of draughts or other local irregularities is excluded, we obtain conditions under which it is fair to apply Newton's law of cooling to the rational correction of losses due to radiation, at any rate for experiments of short duration involving small temperature changes. A method of correction which is both empirical, in the sense that it is based on experiment, and rational, in that it is based on Newton's law, is that proposed by Regnault, and described by his pupils, Pfaundler and Ossouf.

The Regnault-Pfaundler Formula.—The ideal course of most calorimetric experiments can be represented by the continuous line in the following diagram, in which the ordinates represent temperature and the abcissæ time, the lines dividing the curve into three portions representing points of transition from the initial or preliminary period, the principal or heating period, and the final period after the action, the thermal effect of which is to be measured, is complete. In such an experiment the calorimeter, which is in the first place at constant temperature, has its temperature raised by the combustion or other action, and this increased temperature is maintained indefinitely. This state of affairs cannot be attained except by the means adopted by Richards. Actual experiments usually follow the course of either of the broken curves. That is, the experiment is probably started with a temperature rising or falling slightly, owing to differences of temperature between calorimeter and surroundings, and then during the whole of the heating period the actual temperature gradient is lower than the ideal, owing to a continuous and increasing loss of heat to the surroundings. Instead of the curve coming to a steady maximum and remaining horizontal, a short approximately horizontal period at the observed maximum, where for a time loss by radiation, etc., is equal to gain by taking up heat at the end of the reaction, is followed by a cooling period similar to that shown.

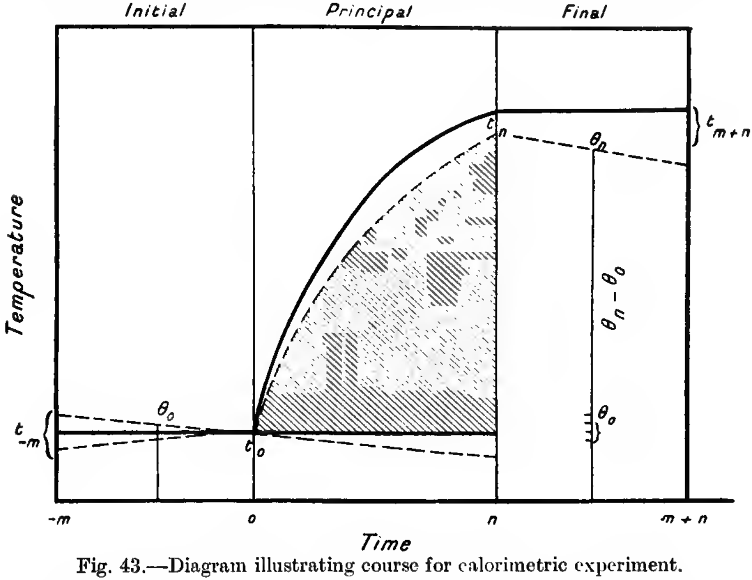

Fig. 43.—Diagram illustrating course for calorimetric experiment.

If we look at the curve representing the actual course of an experiment, we see that during both the initial and final periods it is possible to measure the effect due to surroundings—that is, by observations of temperature at suitable intervals we can take the steady rate of change of temperature during each of these periods of slow exchange. Let the initial period consist of m intervals of whatever duration may be chosen (usually minutes or half-minutes), and the final period (*which does not commence* *until the heating effect due to the action to be measured has been uniformly communicated to the calorimetric substance and the rate of cooling is regular*) consist of a similar number of intervals. The first observation of temperature during the initial period = t_{0-m}, and the last, which is also the first of the principal period, = t_0, the others of the principal period = $t_1, t_2, \ldots\ t_n$, and the last of the final period = t_{m+n}. The mean temperature of each of the initial and final periods will be equal, for the small changes which occur, to one-half the sum of the extreme temperatures (or may be averaged in the usual manner), and the rate of cooling to the difference of temperature divided by the number of intervals—that is,

$$\frac{t_{0-m} + t_0}{2} = \theta_0 \text{ (mean temperature of initial period),}$$

$$\frac{t_{0-m} - t_0}{m} = v \text{ (rate of change of temperature per interval during initial period),}$$

and

$$\frac{t_n + t_{n+m}}{2} = \theta_n \text{ (mean temperature of final period),}$$

$$\frac{t_n - t_{n+m}}{m} = v_1 \text{ (rate of change during final period).}$$

Now, since the rate of change of temperature between a body and its surroundings is proportional to the difference of temperature

$$v_1 - v$$

will be the rate of change for the increase of temperature from the mean of the initial to the mean of the final periods—*i.e.*, $\theta_n - \theta_0$, and the mean rate of cooling for 1° rise during the principal period will equal

$$\frac{v_1 - v}{\theta_n - \theta_0} = k, \text{ the cooling constant.}$$

We are now in a position to make a *rational correction* for the cooling losses during the principal period.

During each interval of this period 1, 2, 3, 4 . . . n the additional loss of temperature will be equal to k, *the cooling constant* multiplied by *the mean excess of temperature over that of the initial period during the interval*, and the total loss during all the intervals will be equal to the total of the excesses of temperature during the whole period × $k = k \Sigma_{t_0}^{t_n}$. Now, the rise of temperature during this period is, and should be, rapid, and it is not reasonable to take the initial temperature of each period as its mean, but if the intervals are sufficiently frequent for the assumption that the portion of the curve corresponding to each interval is a straight line the mean increment will be approximately $\frac{1}{2}$ the rise of temperature, or the mean temperature of each such interval will be $\frac{1}{2}$ the sum of the extreme temperatures, and the mean increment × k equals the loss for each interval. The intervals must be small enough for this assumption to be fairly correct. Our total increment of temperature to be multiplied by k will, therefore, be

$$\frac{t_0 + t_1}{2} + \frac{t_1 + t_2}{2} + \frac{t_2 + t_3}{2} = \ldots \frac{t_{n-1} + \ldots t_n}{2},$$

less n times the mean temperature of the initial period θ_0, since to calculate our losses we must consider *the rise of temperature from the initial period*—not the actual temperature. Since all the terms but t_0 and t_n occur twice in the numerators of the fractions, we now get

$$\frac{t_0 + t_n}{2} + \Sigma_{t_1}^{t_{n-1}} - n\,\theta;$$

that is, the mean rise of temperature during the principal period over the mean of the initial period. Graphically, it is obvious that we have been using the well-known trspezoidal formula to obtain the mean ordinate and to calculate the area of the figure which represents the sum of the increments of temperature. Any other fairly accurate means of doing this can be adopted. The estimation is only for the purpose of a correction, and an error of 5 per cent. is hardly material. Now, the part of our correction due to loss of heat during the principal period $k \Sigma_{t_0}^{t_n} - n\,\theta_0$ becomes

$$\overset{(k)}{\frac{v_1 - v}{\theta_n - \theta_0}}\left(\frac{t_0 + t_n}{2} + \Sigma_{t_1}^{t_{n-1}} - n\,\theta\right),$$

and if the initial temperature is constant no further correction is needed, and v, of course, disappears, as its value is 0. Since, however, at times the initial temperature is either rising or falling, our observed increments of temperature will be either higher or lower, according to whether v will have a *plus* or *minus* value. In either case the loss during the principal period due to this change will be $n\ v$. If v is of *minus* value—*i.e.*, if the temperature of the system is rising owing to outside influences—this apparent loss is strictly a gain, and is, therefore, deducted from the loss as calculated above.

In any case the following complete expression will correct within all errors of experiment, for experiments of short duration, all losses or gains due not only to radiation, but also to any other regular source of error such as evaporation, convection, friction of stirrer.

$$\Sigma \text{ errors} = n\ v + \frac{v_1 - v}{\theta_n - \theta_0}\left(\frac{t_0 + t_n}{2} + \Sigma t_1^{\ n-1} - n\theta_0\right).$$

This value is added to the observed difference of temperature $t_n - t_0$, which is *not* the maximum rise, and, within reasonable limits, should give the same corrected rise of temperature, however far along the cooling curve n is taken, since the losses increase by efflux of time in exact proportion as the value $t_n - t_0$ decreases.

It is usual to let the intervals be of 1 minute duration, for very exact work ½ minute is used. As the whole correction is very small a greater reduction of the interval is not desirable.

The following values from G. N. Huntly will give an idea of the effect of various methods of approximation on the value obtained :—

(1) Planimeter, . . .	0·0258°
(2) Durand, ...	0·0257° (1 min. intervals)
(4) Trapezoidal, . . .	0·0253° (1 min. intervals)
(4) ,, . . .	0·0256° (½ min. intervals)

The points to observe in using this correction are—

(1) That the allowed rise of temperature is within the limits of Newton's law, as illustrated above.

(2) That the intervals shall be small enough, for each experiment, to insure the substantial truth of the assumption that the rise of temperature between any two follows a right line.

(3) That the time of an experiment shall not be so great as to invalidate the above assumptions by making the correction so large that its necessary error is appreciable.

Further, it is obvious that the assumption that the thermometer reading at any moment represents the temperature of the radiating surface must be substantially accurate. Good stirring and, if necessary, a correction for thermometric lag will insure this.

If the heating curves are for a series of experiments of the same class, of very similar form, the areas of the figures included by them are obviously proportional, within small limits, to the maximum rise of temperature—*i.e.*, to the height of the figures—*if the experiments are also of the same duration*—*i.e.*, if the base is common. The correction for radiation then becomes proportional to the rise of temperature. If the loss for the rise of 1° during the whole fixed period is a, then the corrected value of the rise of temperature $t_n - t_0$ becomes

$$t_n - t_0 \, (1 + a),$$

and the gain of *heat* during the experiment becomes

$$\mathrm{E} \, . \, t_n - t_0 \, (1 + a),$$

where E is the water value of the calorimeter. If the value $\mathrm{E}\,(1 + a)$ is used as water equivalent, the calculation becomes a mere multiplication of observed rise of temperature by the altered water equivalent, and, if the latter is determined indirectly, this value can be obtained without any correction.

This simple case only holds good when experiments of the same kind and duration are made starting from a stationary initial temperature. This can be made the usual case in fuel calorimetry, if reasonable care is used.

Various irrational formulæ have been proposed; they possess no great advantage, from the point of view of simplicity, over that of Regnault and Pfaundler, and are far less accurate.

This correction is independent of any constant difference of the temperature between the calorimeter and its surroundings, if this does not differ widely from that of the experiment, since if the temperature of the surroundings be t_s, then

$$\begin{aligned} v &= k\,(\theta_0 - t_s), \\ v_1 &= k\,(\theta_n - t_s), \\ \therefore \; v_1 - v &= k\,(\theta_n - \theta_0 - t_s + t_s), \\ &= k\,(\theta_n - \theta_0), \end{aligned}$$

but obviously if the temperature of the surroundings varies during an experiment an error of greater or less magnitude will be introduced. Nevertheless, a variation of ·2° in t_s in an experiment in which $\theta_n - \theta_0 = 2°$ would only have the effect of increasing or reducing the correction by about 10 per cent., a very small error on the total figure to be corrected.

An example of a calorimetric experiment to which the Regnault-Pfaundler correction was applied may be given as illustrating the method of using this really simple expression.

TABLE XXIX.—Correcting for Minute Intervals.

$$t_n = 19{\cdot}079.$$

Min.		
0,	17·090	Preliminary Period.
1,	·089	
2,	·087	
3,	·085	
4,	·083	
5,	·081	
5.15,	. .	Principal Period.
30,	17·20	
45,	18·00	
6.0,	**18·38**	
15,	·72	
30,	·81	
45,	·99	
7.0,	**19·00**	
15,	·060	
30,	·072	
45,	·080	
8.0,	**19·083**	
15,	·085	
30,	·086	
45,	·086	
9.0,	**19·085**	
15,	·084	
30,	·081	
45,	·080	
10.0,	**19·079**	
15,	·077	Final Period.
30,	·074	
45,	·072	
11.0,	**19·070**	
15,	·069	
30,	·066	
45,	·065	
12.0,	**19·062**	
15,	·060	
30,	·058	
45,	·056	
13.0,	**19·053**	
15,	. .	
30,	·050	
45,	·048	
10.0,	**19·046**	
30,	·041	
15.0,	**19·038**	
16.0,	**19·030**	

$$\begin{array}{r} 17{\cdot}090 \\ 17{\cdot}081 \\ \hline 5)\ \ {\cdot}009 \\ \hline v_0 = {\cdot}0018 \end{array}$$

$t_0 = 17{\cdot}081°$ C.

$\theta_0 = 17{\cdot}086°$ C.

$t_n = 19{\cdot}079°$C.

$n = 5$

$$\sum_t^{w-1} = \begin{array}{r} 18{\cdot}380 \\ 19{\cdot}040 \\ 19{\cdot}083 \\ 19{\cdot}085 \\ \hline 75{\cdot}588 \end{array}$$

$$\begin{array}{r} 19{\cdot}079 \\ 19{\cdot}030 \\ \hline v_1 = 6)0{\cdot}049 \\ 0{\cdot}0082 \end{array}$$

$\theta_n = 19{\cdot}05°$ C.

$$\sum \text{errors} = nv + \left\{\frac{v_1 - v}{\theta_n - \theta_0}\left(\frac{t_0 + t_n}{2} + \sum t_1^{n-1} - n\theta_0\right)\right\}$$

$$= 5 \times {\cdot}0018 + \left\{\frac{0{\cdot}0082 - 0{\cdot}0018}{19{\cdot}05 - 17{\cdot}086}\left(\frac{17{\cdot}081 + 19{\cdot}079}{2} + 75{\cdot}588 - 5 \times 17{\cdot}086\right)\right\}$$

$$= 0{\cdot}009 + \{0{\cdot}0033\,(18{\cdot}08 + 75{\cdot}588 - 85{\cdot}43\}$$

$$= 0{\cdot}009 + 0{\cdot}0033 \times 8{\cdot}238$$

$$= 0{\cdot}009 + 0{\cdot}027.$$

$$\sum \text{errors} = \mathbf{0{\cdot}036°}\ \text{C.}$$

The *observed* rise = 19·079 — 17·081
= 1·998.

The *corrected* rise = 1·998 + 0·036
= **2·034°** C.

If we correct for $\frac{1}{4}$ minute intervals our values for the different signs becomes

$$\begin{array}{lll} \theta_0 = 17{\cdot}086 & & \theta_n = 19{\cdot}05 \\ t_0 = 17{\cdot}081 & & t_n = 19{\cdot}079 \\ v = 0{\cdot}00045 & & v_1 = 0{\cdot}00205 \\ & n = 20, & \end{array}$$

and the expression

$$= 20 \times {\cdot}00045 + \left\{ \frac{{\cdot}00205 - {\cdot}00045}{19{\cdot}05 - 17{\cdot}086} \left(\frac{17{\cdot}081 + 19{\cdot}079}{2} + 356{\cdot}1 - 341{\cdot}72 \right) \right\}$$

$$= ({\cdot}009 + 0265)$$

$$\Sigma \text{ errors} = 0{\cdot}0355.$$

The corrected rise is thus the same as was obtained when correcting at minute intervals.

The Locus in Quo *of Calorimetric Experiments.*—We have considered the influence on a calorimeter of its immediate surroundings, and have definitely recommended an arrangement which will reduce very greatly the result of variations of temperature exterior to these surroundings. It is, however, evident that, at any rate as a counsel of perfection, the calorimeter room should be of a uniform temperature, preferably kept so by means of a thermostat, and that it should have a north aspect, in order that the direct rays of the sun may never reach the apparatus. We may say, at once, that we know that in most technical laboratories, and in many places where research is carried out, such arrangements are impossible.

The following passage from an article by one of us in the *Chemical World* (March, 1912, pp. 75-77) will show that other and more easily adopted means will very much reduce the errors against which a room of constant temperature is intended to guard :—

" It is, of course, highly desirable that calorimetry should be carried out in a fairly large room of constant temperature, but this is not always possible, nor is it absolutely necessary. The writer found that in a small room, heated by a gas fire so that its temperature rose 5° C. during one hour, the mean rise of temperature of a calorimeter protected by a not very large water jacket, externally lagged with white enamelled "cork carpet," and with a further outer metal jacket and intervening air space, was only 0·0017° C. per minute. During the worst period the error due to this cause on a determination, the duration of which would be four minutes, would have been about 0·3 per cent., if corrected for the observed change of temperature during an equal preliminary period, or about 0·7 per cent. if this variation were neglected. If a calorimeter with its water jacket were to be surrounded by another larger water jacket from which it was suitably insulated by an air space and supporting blocks of wood, cork, or ebonite, the effect of variations of room temperature would be extremely small. The water intended for use in the calorimeter itself should be kept in Winchester quarts or other suitable vessels placed close to it."

Since the above article was written the same instrument has been further protected by an external water jacket holding many litres.

IV. The Capacity for Heat of the Calorimetric System.

This must, in all calorimeters of what we shall later designate the still-water type, be known. This system is not homogeneous, in any water calorimeter, since it consists at least of the vessel and the water which it contains. Since the former is hardly likely under any circumstances to have a negligible capacity for heat, it is necessary, in order that correct results may be obtained with still-water calorimeters, that both the amount of water used and the capacity for heat of the apparatus itself should be known. The amount of water may be either weighed or measured. The former is the more exact method, but sufficient accuracy (say 1 in 1,000) can be obtained by the latter, especially if proper correction be made for the effect of temperature on the mass and the specific heat of water. This is not necessary for ordinary work where an accuracy, say, of ·5 per cent. is all that is aimed at. The heat capacity of the rest of the calorimetric system can be determined in either of the following ways :—

(1) By calculation of the capacity of the various parts.

(2) By communicating a known amount of heat to the calorimeter with a suitable amount of water in it. This may be done (*a*) by burning a known amount of fuel of known calorific power ; (*b*) by passing an electric current of known strength through a resistance for a known time.

(1) *Calculation.*—By the first method, if a, b, c, d . . . be the respective weights of the various parts of the calorimeter, and l, m, n, o . . . the specific heats of the materials com-

posing these parts, the total capacity of the system w will be

$$w = a\,.\,l + b\,.\,m + c\,.\,n + d\,.\,o \;\ldots$$

The question may be raised, What should be included as part of the calorimeter for this purpose? Everything which is within the vessel or is in metallic contact with it, and is likely to take part fully in the change of temperature caused by an experiment. That is, vessel, stirrer, so far as the non-conducting holder or sleeve, combustion chamber, and thermometer are included, but not the ebonite or wood supports or any ebonite lid, handle of stirrer, or the like. The portions of the calorimeter vessel and stirrer, etc., above the water level are reasonably considered as part of the system, as, owing to the good conduction of heat by metals, especially copper, the temperature is practically uniform throughout.

The weak point of this method is that it is dependent on the determination of specific heat of perhaps several substances, which may not be very reliable. The effect of this source of error may be reduced by making W, the water content of the vessel, great relatively to w, the heat capacity of the metal, etc., parts—*i.e.*,

$\frac{w}{W + w} = \frac{1}{10}$, an error of 5 per cent. in the value of w affects the result 0·5 %

$= \frac{1}{20}$. ,, ,, ,, ,, 0·25 %

It is well to take values for the specific heats of the materials corresponding as near as may be to the temperature of working —*i.e.*, if values between 5° and 30° and between 5° and 100° are available, choose the former; as the latter will be too high— *e.g.*,

Copper, . . − 2° − 22° = 0·0915 0° − 100° = 0·094.

(2) (*a*) *A combustion calorimeter* can be calibrated by burning a known volume of pure hydrogen, carbon monoxide, or any gas or, if convenient, a solid or liquid (these would be weighed) of known calorific power. If q calories represent the amount of heat evolved in the combustion of unit volume of gas, and v equals the determinate volume chosen, then

$$q\,.\,v = t\,(W + w),$$

where t = the rise of temperature due to the experiment.

Then w the only unknown $= \frac{q\,.\,v}{t} - W$.

This chemical method is clearly dependent on the accuracy with which the calorific value of the standard substance is known, on its purity, and on the accuracy with which it is measured. We do not consider it as suitable for gas calorimeters as the former method, although the calorific values of hydrogen and carbon monoxide are fairly well known. It is good enough, with care, for technical work. For bomb calorimeters where solids can be used the following substances possess well-defined heats of combustion :—

TABLE XXX.—Heats of Combustion.

Benzoic acid, ...	6,325 calories per gramme.
Naphthalene, ...	9,668 ,, ,,
Cane sugar, ...	3,954 ,, ,,
Cellulose, ...	4,208 ,, ,,

(*b*) *The electrical method* involves the following arrangement :— An electric current is passed through a suitably insulated resistance, preferably a strip of constantan, manganin, or other alloy with a low temperature-coefficient for change of resistance. The strength of the current is so regulated that in a few minutes a rise of temperature of the same order as that which is likely to be measured is produced. A standard cell and potentiometer to measure the E.M.F., and a resistance box and bridge to measure the resistance, will determine the amount of electricity passing in unit time. If the time and the corrected rise of temperature be noted, then

$$\frac{(\text{E.M.F.})^2}{\text{R}} \times \text{time in seconds} = \text{Watt seconds.}$$

The 15° small calorie = 4·19 Watt seconds (about)—*i.e.*, 1 Watt-second = 0·2387 calorie—so that

$$\text{Watt-seconds (calories)} \times 4{\cdot}19 = t \times \text{W} + w;$$

and

$$w = \frac{\text{calories}}{t} - \text{W}.$$

Fischer and Wrede used 4·177 (1 Watt-second = 0·2394 calorie).

The relative merits of the various methods of determining the water equivalent of still-water calorimeters may be considered. In the first place, the method of calculating from the specific heats and weights of the various parts is sound, provided (1) the specific heats of the various substances are sufficiently known, (2) the parts can be weighed separately with sufficient accuracy, (3) the unimmersed portions of the calorimetric system are either negligible, determinable, or are composed of materials of known high conductivity. For instance, a glass jar, although its specific heat may be fairly well known and weight be easily determined, will always present a difficulty by reason of the upper portion above the water line, since the conductivity of glass is low and the mass of the upper portion is not easy to determine (although this can be done), and even then it is doubtful how much of it will ever reach the temperature recorded by the thermometer. On the other hand, the glass and mercury of a thermometer presents less difficulty, since a solid stem thermometer will have a fairly uniform capacity for heat of about ·45 calorie per cubic centimetre. Now, if as much as 20 c.c. of a thermometer are immersed in the water and the heat capacity of the immersed portion is taken as = 9 grammes of water, the total result of an error of 10 per cent. in this estimation will only be ·09 per cent. if the calorimetric system has a capacity of as little as 1,000 grammes of water. A composite thermometer of the enclosed pattern presents a greater difficulty, and if a maximum value for its heat capacity is not sufficient a calorimetric experiment must be made.

The combustion of known amounts of substances of known heat of combustion is a most convenient method, and is very exact, but it must be remembered that the values are dependent on calorimetric determinations, which were made with a calorimeter, the water value of which must have been determined in some other way. It is only a *secondary* method, and should not be used for the determination of new values for thermo-chemical research, unless it is made clear to what the determinations are ultimately referred.

The electrical method depends on the value of Joule's equivalent. This in turn depends on the determination of electromotive force. As to this some uncertainty exists, more due to the adoption of a conventional value for the E.M.F. of the Clark cell than to any other cause. Professor Callendar and the workers at the American Bureau of Standards agree within ·0001 volt in the value of the E.M.F. of this cell, which they make 1·4334 and 1·4333 respectively. Callendar repudiates the idea that his values for J were uncertain to the extent of more than 1 in 1,000. Combining the values of Rowland, Reynolds and Thornby, Barnes and Callendar, and Barnes, it may be taken that the value

$$J = 4{\cdot}180 \text{ S Joules gramme-degree C. (Callendar)},$$

when S = the specific heat of water (see Table XVII.) is good to 1 in 4,000, so that this represents the uncertainty in the heat equivalents determined by this method. Those who have standard cells, calibrated resistances, and a potentiometer available may well use this method. Determinations of the water equivalent by this means can be made for private workers at the National Physical Laboratory.

This method, and the secondary method of combustion of substances of known heat of combustion, have the theoretical advantage over the calculation from the heat capacity of the parts that they are the result of experiments of a class similar to those for which the calorimeter will be used, and that the effect of the lag of the bomb due to slowness of heat exchange between the substances within it and the water outside is eliminated. The value of this is extremely small (*cf.* Jaeger and von Steinwehr, *Zeits. für Physik. Chem.*, vol. liii. (1905), p. 153, who have very carefully studied this and other such subtle points).

G. N. Huntly has pointed out * that when a Beckmann thermometer is used the correction for the varying value of a degree can be eliminated by using varying water equivalents for the different ranges of temperature, if a calorimetric method is used for the determination of the water equivalent. It is also clear that whatever the error of the value of the degree of a thermometer of any kind it can be eliminated, since the value of the water equivalent will vary in inverse value to that of the degree.

The thermal capacity of a copper calorimeter with no very heavy parts can easily and accurately be determined by the weight method, since the specific heat of copper at ordinary temperatures is now well known (*cf.* p. 146), and its conductivity is high. A fairly large error in the capacity of the metal part of the system will have a small effect on any calorimetric experiment, since a large quantity of water is always used. For instance, if the total capacity of the metal and water is equal to 2,000 grammes of water, and the metal alone has a capacity equal to 100 grammes of water, an error of 5 per cent. on this will only amount to ·25 per cent. on the whole. It should be noted that

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* *Journ. Soc. Chem. Ind.*, 1910, p. 918.

in this case the metal, if copper, would weigh 1,100 grammes, and further that the specific heat of copper is known to about 1 per cent., which would reduce the error to ·05 per cent. When, however, we come to consider bomb calorimeters, the case is rather different. The bombs are often made of alloys of uncertain specific heat, are lined with porcelain or a noble metal, snd, of course, are very heavy, so that their thermal capacity is a considerable proportion of that of the whole system.

CHAPTER VII.

THE CALORIMETRY OF GASEOUS FUEL.

I. Measurement of Gas—Necessity for Volumetric Methods—Holders—Meters—Solubility of Combustible Gases in Water. **II. Still-Water Calorimeters**—Thomsen's, Favre and Silbermann's, Berthelot's, Hempel's, Fischer's, Coste's—Use of Bomb Calorimeters—Corrections to Constant Pressure. **III. Flow Calorimeters**—Principles of Action—Results Independent of Capacity for Heat of Calorimeter—Fundamental Requirements—Dry and Wet Governors—Collins' Simple Governor—Water Supply—Two Classes of Flow Calorimeters—(1) Junkers', Modified Junkers'—(2) Boys'—Mode of Testing Calorific Power. **IV. Calculation from Heats of Combustion and Analysis.**

I. Measurement of Gas.

Necessity for Volumetric Methods.—To determine the amount of thermal change accompanying any physical or chemical action it is necessary to measure, not only the amount of the thermal effect, but the mass or masses of substances which are producing it. If these are liquid or solid, the most convenient means of determining their mass is the balance. As, however, we have elected to consider, in the first place, gases, we shall find that a measurement of volume with the necessary auxiliary measurements of temperature and barometric pressure is usually the most convenient way of determining their mass.

Holders.—The volumes of gas which must be burnt to obtain a suitably large thermal effect in any ordinary water calorimeter are much greater than those usually manipulated in the analysis of gases, and rather special means must be adopted for their measurement. We can collect some of the gases to be examined in a small holder and burn a known volume, either the whole volume in the holder or a definite portion, or may use a continuous meter for measuring a constant stream of gas. If the composition of the gas be known, we may burn a convenient, but unknown, amount and weigh the products of its combustion, calculating the original mass therefrom. This latter plan is not usually (if ever) adopted for technical purposes, although it is most often used for research.

When relatively small quantities are to be burnt, as in still-water calorimeters, the simplest plan is to collect a sample of gas in a holder, and then to deliver it through the burner of the calorimeter. Combustion can be started and when a definite volume of gas is left in the holder the burner is transferred to its place in, or under, the calorimeter, so that the heating effect due to the known residual volume of gas is measured.

Owing to the wide surface of the confining liquid, a measurement of gas is not very easily made with accuracy by the use of marks on the side of the vessel, as errors of several units per cent. can be made in this way. Various devices can be used to increase the accuracy of such measurements. One involving the use of an auxiliary side tube has been adopted by Messrs. Simmance and Abady; in another, adopted by one of us, the measurement is made from a central point, the contact of which with the liquid is very easily observed.* It is subject to errors of very small magnitude: on the volume to be measured in this case it amounts to only 0·1 per cent. or less.

Meters.—In flow calorimeters, where a considerable amount of gas must be burnt to obtain a state of equilibrium before an observation can be made, it is usually necessary to use a wet gas meter. These are made of a series of small gasholders of suitable shape arranged radially around a central hollow axle in a closed vessel partly filled with water in such a manner that each as it fills rises in the water until the gas which it contains escapes into the upper part of the casing. A circular motion is thus communicated to the axle and holders, as an outlet pipe for the gas is arranged in the upper part of the outer vessel. This motion is conveyed by means of the axle to a pointer, which indicates the amount of the motion on a dial or, in some cases, a series of dials. The divisions of the dial very closely approximate to equivalent fractions of the volume of the series of holders, but it is better for accurate work to measure only complete revolutions of the spindle.

It is usual, in England, to let one revolution correspond with one-twelfth of a cubic foot, as then the attainment of the usual standard rate of burning 5 feet an hour is indicated by the time of one revolution being one minute. (In America one-tenth of a foot is more usual; and on the Continent 3 litres is common.)

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* Mr. Huntly has used this device in a gas analysis apparatus (see p. 27).

Obviously, for the accurate working of the meter, the amount of water in it must be maintained at a suitable level. This can be done with some approximation to accuracy by having a scratch made on a side window and adjusting to this. It is better to have a depending pointer similar to that used in the holder mentioned above. The most satisfactory plan is to have a small standard holder which will deliver such a volume of gas as may correspond to one revolution or an aliquot part of a revolution of the meter hand. In England a $\frac{1}{12}$ cubic-foot bottle, as designed by the Metropolitan Gas Referees, is used, and in Germany Junkers' 1-litre bottle. The former apparatus *delivers* $\frac{1}{12}$ cubic foot under a slightly increased pressure, the latter *collects* 1 litre under slightly reduced pressure.

In all cases the observed volumes must be corrected by means of the gas laws to standard temperature and pressure. For statutory purposes, in England, these are 60° F. and 30-inch bar., the gas being measured moist. Tables of "tabular" numbers are convenient for this purpose.

The solubility in water of the constituents of combustible gaseous mixtures, such as coal gas (*cf.* p. 14), introduces a somewhat irregular source of error in both meters and holders, but it is usual to allow the water to become saturated before a meter is used for the measurement of gas. This can also be done in some holders. In other cases a correction can be made. The use of mercury would remove this error, but the cost and inconvenience of manipulating some litres of mercury could not be incurred in instruments used for technical purposes (although mercury is necessary for the most exact work). Hydrocarbon gases are only very slightly soluble in a mixture of equal volumes of glycerine and water. This, in many cases, may be used. Its vapour tension is only slightly less than that of water. The uncertainty of the magnitude, which is not great, of the error due to solubility of gases in water is complicated by changes of temperature, which must lead to exchanges between the water and the gas passing over it, even although the former has been saturated at some other temperature. This is one of the many circumstances which make the use of a room of equable and moderate temperature most desirable for calorimetric work. A fairly large room facing north and maintained at a temperature near 60° F. (= 15·5° C.) is best; when this cannot be obtained great care must be taken in using calorimeters, more especially those which are not provided with water jackets. We do not say that such a room is necessary; in fact, it is often unobtainable, but in default some judgment must be used in arranging apparatus (*cf.* p. 189).

II. Still-Water Calorimeters.

The classical work of Julius Thomsen was carried out in a calorimeter of the form shown in Fig. 31. A metal cylinder holding a known volume of water and itself having a known capacity for heat, contained within it a platinum combustion chamber in which the gas to be examined was burned in an excess of oxygen by means of a suitable burner. The products of combustion escaped through a long spiral tube of platinum and were analysed, the amount of gas burnt being calculated from the results. A thermometer registered the change of temperature during an experiment, and a stirrer kept the water at uniform temperature. The calorimeter was insulated upon three ebonite points, and was protected from draughts by a cylinder of ebonite concentric with it. Here the arrangement for protecting the calorimeter is not such as would now be considered satisfactory, but the plan of burning gases at a constant rate by means of Mariotte's arrangement was good.

Favre and Silbermann * had previously used a somewhat similar apparatus, which, however, was inserted from above into the calorimetric vessel, and was "lagged" with swansdown and surrounded outside this with a water jacket. The amount of gas burnt was estimated from the examination of the products. Here, again, the externals of the calorimeter vessel were not such as are now considered good.

Berthelot used a somewhat similar vessel and spiral tube, but made of glass. (Stoecker and Rothenbach have lately suggested the use of a vessel very similar to this.) They both use water jackets of modern form.

All these forms of apparatus are quite good, provided a proper excess of oxygen is used and the calorimeter vessel is suitably large and properly provided with stirring apparatus, as well as with protective jackets, but none are, in practice, used for technical purposes.

W. Hempel introduced, in 1901, an oxygen calorimeter for gases, which has good features, but is hardly convenient for

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* *Ann. Ch. Phys.* (3), vol. xxxiv., p. 357; vol. xxxvi., p. 5; vol. xxxvii., p. 406.

ordinary laboratory or works use, or sufficiently accurate for research work. The gas (2 to 3 litres) is burned with oxygen in a special burner, which is pushed up a small copper cylinder inside a glass one holding water. A hydrogen flame is used to ignite the gas, and the instrument is calibrated by means of pure hydrogen. No correction is made for radiation, and no precautions are taken to guard against loss of heat from this or other causes. No doubt if the calorific power of a gas is not very different from that of hydrogen the results obtained are fairly accurate, but in the case of coal gas the loss of heat by radiation would be greater and with producer gases less than with hydrogen. In an example given the rise of temperature for a reservoir full of hydrogen was 10·838°, which seems to be a rather large rise to measure in an unjacketed vessel. This instrument is quite unprotected, and the use of glass as an external surface for the calorimeter is very undesirable. It cannot be said that in this respect it is well designed. A whole vessel full of gas must be burnt, as means are not provided for measuring a portion.

A more convenient class of still-water apparatus for technical work comprises those instruments in which free combustion in air is adopted instead of using a current of oxygen. By doing this some amount of auxiliary apparatus is dispensed with and manipulation is simplified. On the other hand, the mass of the "spent gases" is very largely increased by the nitrogen of the air used and appreciable loss, due principally to aqueous vapour in the products, is caused thereby, and a small and probably negligible error is introduced by the formation of oxides of nitrogen. A very simple and, we believe, very inefficient instrument of this kind has been described by Graefe, who burns a measured volume of gas under a tall cylindrical vessel containing water and pierced with a central chimney fitted with a central metal rod carrying wire-gauze discs, which act as baffles and check the flow of gases through the instrument. As both measuring and cooling arrangements are weak, the results obtained by the instrument are very low.

Fischer has designed two calorimeters which, so far as the burning and cooling arrangements are concerned, appear to be very good. The products are thrown against the sides of the lenticular passage by means of circular copper plates notched or scolloped on their circumferences. It appears that a meter is generally used for measuring the gas burned in these instruments, but apparently a litre holder can be supplied. Both forms are jacketed; in one a wooden and in the other a brass vessel surrounds the calorimeter, from which it is separated by an air space.

Coste.—One of the authors has designed a calorimeter of this type, which is described by him and B. R. James (*Journ. Soc. Chem. Ind.*), and in the *Calorific Power of Gas*, pp. 170-9.

Use of Bomb Calorimeter for Gases.—Very satisfactory determinations of the calorific power of gas can be made in a bomb calorimeter. An instrument of this kind, but used only at low pressures, was employed by Andrews, of Belfast, for gases (*cf.* p. 150). The calorimeter bomb is a thick-walled metal vessel with a suitable gas-tight cover fitted with a valve or valves. Gases or other bodies can be burnt instantaneously in it by means of oxygen, which is introduced under pressure by means of the valve. Combustion is effected by a spark from a coil passing between the bomb cover and an insulated conductor, as in Berthelot's original bomb (Fig. 33), or by the heating effect of an electric current on a thin wire of platinum or, in some cases, iron, as in the Mahler-Krocker and the Bryan-Donkin bombs (Figs. 58 and 59). The arrangement of the bomb in the calorimeter vessel is clearly shown in Fig. 59.

We have found that in the Bryan-Donkin bomb good results can be obtained without much trouble by carefully determining the capacity of the bomb, and then alternately exhausting and filling it with gas two or three times. The bomb is placed in a large vessel of water, the temperature of which is taken, and when finally filled the valve is opened for a moment to equalise the pressure, which is always a little above that of the atmosphere. The barometer is now read and a suitable excess of oxygen—about four times the volume of the gas—introduced. The bomb is placed in the calorimeter, as shown, and the mixture fired by passing through the fine platinum wire a current which will heat it to incandescence. A sharp "snap" or "yelp" is heard, and the temperature immediately rises. As the rise may be under 1° C., it is well to use all proper precautions and corrections. A Mahler-Krocker bomb which has wash-bottle fittings is much more convenient for gas, as it is more easily filled.

Correction to Constant Pressure.—It must be borne in mind that the results of combustion in the bomb are obtained on gas kept at constant volume, whereas those in ordinary calorimeters are at constant pressure.

On such a combustion as

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

a diminution of *volume* occurs, owing to the condensation of water, if the pressure be kept constant, as in ordinary flaming combustion ; but if the volume, as in a bomb, be kept constant then an expansion of the residual gas must take place for the whole volume to be filled ; work is done by the gas, and the result is lower by the amount of work done.

For 1 gramme molecular volume the loss is

$$\left(1 + \frac{\text{vols. of hydrogen in 1 vol. of gas}}{2}\right) 0{\cdot}58 \text{ Calorie,}$$

for 1 cubic foot 0·58 becomes 0·68.

A sufficiently good approximation for town gas is obtained by assuming (a valid assumption) that the difference between gross and net calorific power is one-tenth of the gross. This figure divided by 13 will give the volume of hydrogen in 1 volume of the gas.

The formula becomes, therefore,

$$\left(1 + \frac{\text{gross calorific power}}{260}\right) 0{\cdot}68 \; ;$$

probably for most such gases

$$1{\cdot}5 \times 0{\cdot}68 = 1{\cdot}02,$$

or *one calorie* to be added to the bomb results in making them comparable with those of other calorimeters, is a suitable correction.

III. Flow Calorimeters.

Principle of Action.—It has already been indicated that when a practically unlimited amount of gas is available—that is, enough for, say, an hour's consumption at the rate of about 5 cubic feet per hour—a type of calorimeter can be used in which the burning of gas at a constant rate is made to heat a constant stream of water, the increase of temperature of the outlet water over that entering the instrument being a measure of the calorific power of the gas for the same ratio of gas to water. If the ratio varies, due allowance for this must be made. The principle is in effect the same as that of the still-water type.

$$\text{Vol. of gas} \times \text{calorific power} = \text{mass of water heated} \times \text{rise of temperature}$$

$$\therefore \text{Calorific power} = \frac{\text{mass of water heated} \times \text{rise of temperature}}{\text{volume of gas}};$$

only, unlike the still-water instruments, it is of no use taking readings until a state of permanent equilibrium is obtained—*i.e.*, the water in its passage through the instrument and the various parts of the calorimeter must assume the temperatures which are consistent with the attainment of a uniform maximum increase of temperature, for the conditions then prevailing, of the outlet water. There is no attempt to secure temperature homogeneity throughout the calorimeter, as is done, by stirring, in still-water calorimeters.

The results obtained with a flow calorimeter are independent of its capacity for heat, which need not, therefore, be determined. The most serious effect of a high-water equivalent is to delay the attainment of a state of equilibrium.

If we could realise the simple conception of a constant stream of burning gas communicating all the heat generated by its combustion to a constant stream of water, without any intermediate appliances, we should at once obtain the maximum heating effect on the water, and the calorific power of the gas could be calculated from the following equation, in which the amounts of gas and water are referred to the same interval of time :—

$$\text{Calorific power} \times \text{amount of gas burnt} = \left\{ \begin{array}{l} \text{rise of temperature of water} \times \text{the mass} \\ \quad \text{which passes through the instrument} \\ \quad \text{during the combustion of the} \\ \quad \text{measured volume of gas} \times \text{its mean} \\ \quad \text{specific heat for the temperature} \\ \quad \text{interval.} \end{array} \right.$$

Since, however, suitable means must be provided for a sufficiently large surface of contact between the cooling water and metal heated by the passage of the gaseous products of combustion it is not possible to obtain this rapid heating. If we still assume that a uniform addition of heat to the system, calorimeter + flowing water, takes place, we shall find that the temperature of the outlet water rises slowly to a maximum, which is determined by the calorific power of the gas and the relative rates of flow of water and gas, and, of course, by its initial temperature. The calorimeter itself is not, in this type, of uniform temperature, but the temperatures of the various parts will rise until the temperature gradients are constant. By this time, unless the instrument is very badly designed, practically *all the heat produced by burning the gas will be communicated to the water* for the amount required by the calorimeter will have been reduced to that lost by radiation, etc., from its outer surfaces. This amount can be so reduced by suitable construction as to be of a very low order of magnitude. As the temperature of the exit water is no longer rising, the heat leaving the instrument must be equal to that imparted to it. The only source of loss, other than the water stream and the exterior of the instrument is the stream of cooled products of combustion. This, again, is small, although not altogether negligible.

An early instrument, the first technical gas calorimeter in fact, was designed by the late F. W. Hartley. The water flowed from a small cistern through a Coffey still-head and around the square combustion chamber. It could be measured or weighed, and the gas was burned in a small burner at the lower part of the instrument. Thermometers registered the temperatures of the inlet and exit water and the exit gases.

Fundamental Requirements.—Before considering the construction of any instruments now actually in use, we must pause to consider the two fundamental requirements of a flow calorimeter.

A constant stream of gas burning at a (nearly) uniform rate.
A constant stream of water passing at a (nearly) uniform rate and of a (nearly) uniform temperature.

The measurement of gas has already been described, a meter is, of course, used for instruments of this type. A uniform rate of flow is, however, necessary. This can be obtained within very small limits by the use of a gas governor.* Two forms of this instrument are made.

Dry or diaphragm governors are arranged so that the pressure of gas passing through a shallow drum, the upper part of which is a loose greased-leather septum, shall lift this septum, and with it a conical or hemispherical valve, which, in rising, is brought closer to its seating, and by decreasing the aperture reduces the flow of gas. An increase of gas pressure in the main raises

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* A governor will only act as a pressure regulator. The flow of gases is determined by their density as well as by the pressure they are under. Hence governors do not insure a constant flow of gas of variable composition.

the valve and checks the pressure of the issuing gas ; a decrease allows the valve to fall, and gives a wider passage for the gas. The smaller governors of this kind have weighted metal discs on the leather diaphragms ; the larger have an adjustable spiral spring. Small double dry governors, consisting of two arranged in series, are convenient and efficient—within reasonable limits for initial pressure.

Balance or wet governors act on the same principle of the variations of pressure of the gas opening or closing the aperture between a valve and its seating; but, instead of a leather diaphragm, a bell or small gasholder floating in water and attached to a beam, the other side of which is weighted to balance it, carries the valve. The range of the governor can be adjusted by varying the weights on the far side of the beam. Frequently such a governor is used after a large diaphragm governor, which, in such a case, is called an "initial governor." Where the pressure is great a mercurial governor working on the same principle is used. As an inch of mercury withstands as much pressure as 13 to 14 inches of water, it will be understood that for high pressures mercurial governors are more compact than those in which water is the confining fluid.

Collins' Simple Governor.—Mr. S. H. Collins, M.Sc., of the Armstrong College, Newcastle, has described a useful governor, which can be made in the laboratory.

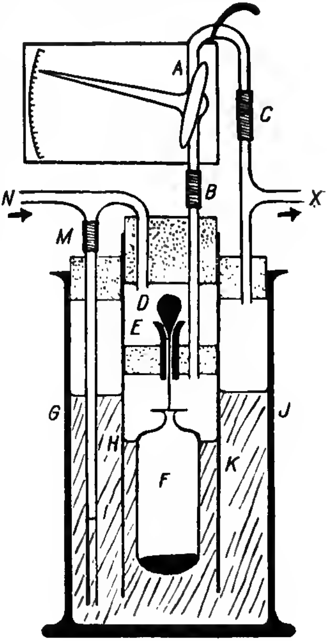

Fig. 44.—Collins' governor.

A (Fig. 44) is a glass tap with long pointer and scale mounted on a wooden block, *B*, *C*, and *M* are rubber connections, *D* is a piece of glass rod drawn out with a long tail, *E* is a piece of glass Sprengel tube blown with a bulb at one end and then ground down, *F* is a float weighted with mercury and having a platform of flat glass cemented on, *K* is a piece of wide glass tube, and *J* is a glass cylindrical jar. The point of entry of the gas is at *N* and the point of exit at *X*. When in work, the pressure of the incoming gas depresses the water in the pressure tube to *I*, but the gas does not pass through this tube, but passes on into the chamber containing the valve made by *D* and *E*. The rate at which the gas passes through this valve depends upon the position of the float *F*, which is kept hovering about a position determined by the level *H* according to the exact dimension of the instrument. The level of water *G* is dependent on the amount of water placed in the jar *J*, and is easily adjusted before operations commence. The height *G H* is in consequence fixed once for all, the height *G I* shows the pressures of the incoming gas, the height *H I* shows the surplus pressure which is being got rid of by the valve *D E*, and which is liable to variations due to irregular action in the other parts of the apparatus.

As the difference of pressure on the two sides of the tap is kept constant and the tap is fixed by trial, both pressure and resistance are constant and, therefore, current is constant also, unless the specific gravity of the gas should vary. Within certain limits the pressures and resistances before *N* and after *X* may vary, but the current of gas remains constant.

The records from twenty-two actual runs with this instrument show an average flow of 10·05 ± ·22 litres of gas per hour; when 10 litres was the flow required. This rate includes stopping and starting and long intervals of one or two hours without attention.

Water Supply.—Water from the mains is usually of almost constant temperature. We found in a house in the West Central district a variation of less than ·1° C. in an hour, or less than 1·0° C. in a day. In winter this water is, however, usually at a much lower temperature than that of any working room, and an error, the effect of which will be considered later, is caused.

A cistern in the room, preferably arranged so that the inlet may be closed during an experiment, and, therefore, no mixing with water of different temperature from that of the room shall occur, is probably the best, or at least the simplest, arrangement. Other devices for equalising the temperature of the water and the surroundings of the calorimeter have been described by one of us and B. R. James.* They are, first, raising the water to the temperature of the room by a heating coil, followed by a cooling coil. This was found to be very efficient. Another simple

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* *Journ. Soc. Chem. Ind.*, p. 68, 1911.

method is to surround the instrument with an annular metal vessel, through which the water circulates before reaching the inlet thermometer. The error due to the absorption or radiation of heat may also be corrected by considering the thermometer readings when water is flowing at the desired rate, but *no gas is burning,* as index or zero errors, and using the observed increased difference between inlet and outlet.

Constancy of flow is obtained by maintaining a constant head of water, as will be shown.

Two Classes. — Flow calorimeters may be considered as of two classes—(1) those in which the passage of both water and gas through the apparatus is, by one or many paths, very short, and rather of the nature of a parallel arrangement; and (2) those in which the water flow is through a long tube around which the air slowly passes. The former class includes most of the flow calorimeters, Junkers' being both the best and the best known; Boys' and one of Simmance & Abady's instruments are the only representatives of the latter.

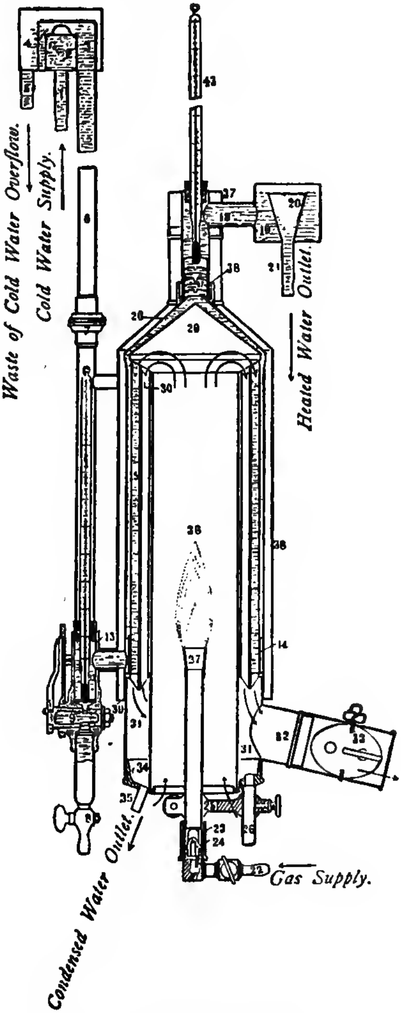

Fig. 45.—Junkers' calorimeter (vertical section).

Junkers' calorimeter (Figs. 45 and 46) is one of the earliest and best of its kind. Its form is that of a tall cylindrical vessel with a central cylindrical combustion chamber opening into a series of small tubes, through which the spent gases pass downwards and from the instrument. Water circulates in the vessel and between the tubes. Its path is from the bottom of the vessel upwards, and the path of the gases is upwards in the combustion chamber and downwards in the tubes, so that they leave the instrument at a temperature approximating to that of the entering water. The temperature of the inlet and outlet water can be observed by suitably placed thermometers, also that of the exit gases. A well-designed Bunsen burner is used for burning the gases, and is fitted with a special nozzle for producer gas. The flow of water is maintained at a constant rate by the plan of working from a fixed head secured by a weir overflow to a fixed outflow; then, as the head is constant and resistance to flow can be regulated by a quadrant tap, the position of which can be recorded on a scale, it is possible to obtain any convenient rate of flow, and to maintain it for any reasonable length of time.

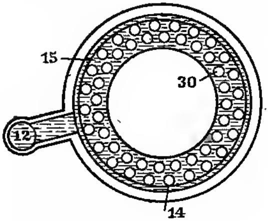

Fig. 46.—Junkers' calorimeter (transverse section).

A series of baffles is provided under the outlet thermometer for equalising the temperature of the water as it is about to leave the calorimeter. This is the only point where it is necessary to maintain a steady temperature of the heated water.

The water flowing through the calorimeter during any desired number of revolutions of the meter hand can be collected. If during two revolutions of a $\frac{1}{12}$ cubic foot meter 2,200 c.c. of water were collected, and the mean temperature of the entering water was 15° C., and that of the outlet 25·1° C., the calorific power, uncorrected for temperature and pressure, would be obtained, thus,

$$\tfrac{2}{12} \times \text{calorific power} = (25{\cdot}1 - 15{\cdot}0) \times 2{,}200$$

$$\therefore \text{ calorific power} = \frac{10{\cdot}1 \times 2{,}200 \times 12}{2} = 133{\cdot}3 \text{ Calories.}$$

$$133{\cdot}3 \times 3{\cdot}968 = 528{\cdot}9 \text{ B.Th.U.}$$

A modified form of Junkers' calorimeter (Fig. 47), with swinging

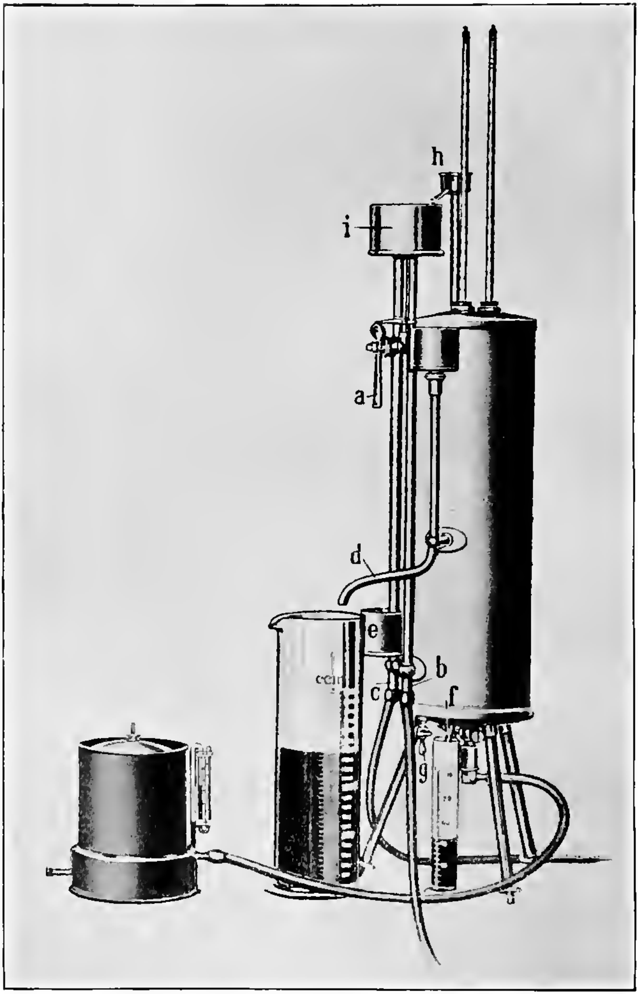

Fig. 47.—Junkers' Calorimeter (new pattern).

arm for the exit water (which when a test is not being made can discharge into an overflow, instead of into the sink), and with the two water thermometers on the same level, has been introduced, and should be a little more convenient than the old pattern. This pattern does not have air tubes, but two concentric water vessels with the annular space between packed with corrugated metal. In both forms the water formed by the combustion of the gas drains into a circular gutter; after the inner surfaces of the tubes, etc., have become thoroughly wetted and the flow regular this water can be collected and its amount determined by measuring. One gramme (1 c.c.) of water vapour condensed and cooled to the ordinary temperature gives out about 0·6 of a Calorie.

Actually for 15° C. (= 60° F.) $0{\cdot}540 + \frac{100^\circ - 15^\circ}{1{,}000} = 0{\cdot}625$ K.G. Calories. So that if during the combustion of 1 cubic foot (= 12 revolutions) of the gas considered above, we collected 21 c.c., the amount of the 133·3 Calories per cubic foot due to the condensation of the water is $21 \times 0{\cdot}62 = 13{\cdot}0$ Calories.

Now, if this were not condensed, we should be measuring the *net* calorific power, so that the *net* calorific power of the gas is the gross $133{\cdot}3 - 13{\cdot}0 = 120{\cdot}3$ calories. It is usually found that the net calorific power of coal gas, or the mixture of this gas with carburetted water gas frequently supplied, is about nine-tenths of the gross. The figures given represent the average of many results, and illustrate the truth of this statement.

Sugg and Simmance & Abady have both designed calorimeters which may be considered as modifications of Junkers' form. The principal difference is that in these the hot gases are cooled by flowing through annular spaces between annular water vessels, instead of through a series of tubes as in Junkers' form. A very good change-over device for the water is adopted in Sugg's instrument. Simmance & Abady have superseded their original instrument by one of a very different type.

Boys' calorimeter (Fig. 48) was designed by Mr. C. V. Boys, in his capacity as a Metropolitan Gas Referee, for the purpose of official testings in the County of London. It is described in the *Proceedings of the Royal Society* (A., vol. lxxvii., 1906, p. 122) and in the *Notification of the Metropolitan Gas Referees.* Its peculiar feature is that, instead of the products of combustion passing in parallel through a series of short paths and surrounded by water, a slow and perfectly free stream of gas passes around

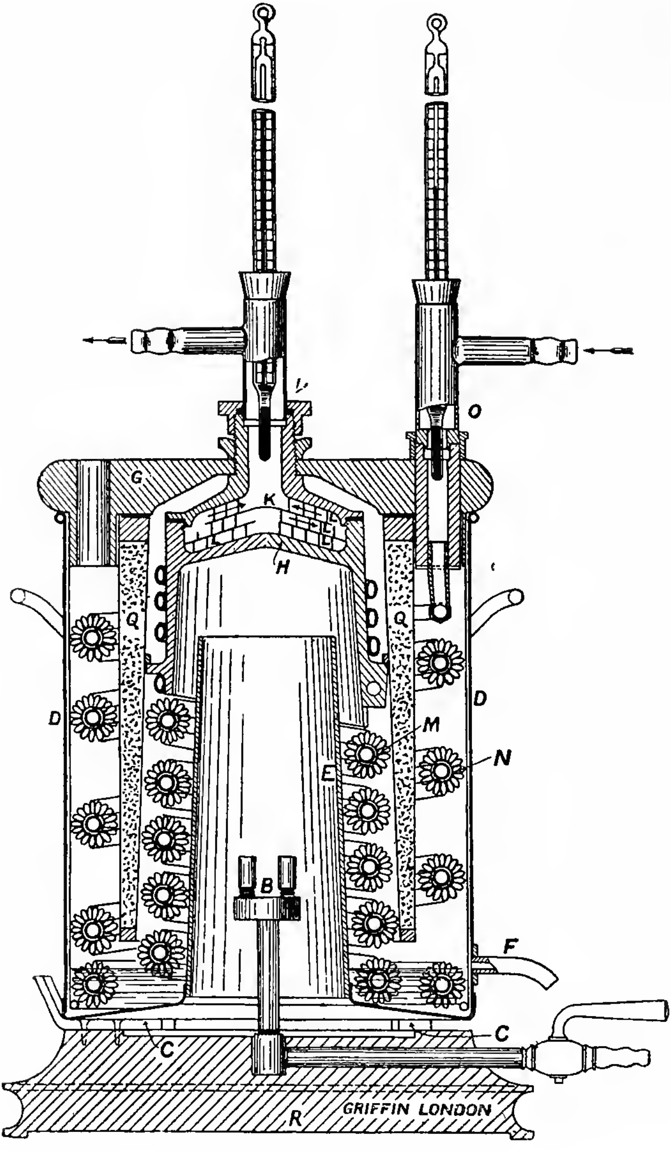

Fig. 48.—Boys' calorimeter.

a long coiled-up water pipe, which is surrounded with wire coils or other devices to ensure very rapid transmission of heat from the gases to the cold water in the pipe. The section in Fig. 48 will show the construction. The gas is burned from two ordinary "union" jets giving a short, yet fully oxidised, flame. A vessel, partly filled with water, forms a chimney which steadies the flames and allows a suitable draught to flow under the vessel, which is lifted from the base plate by three blocks or feet. The gases then pass under a thick brass mixing box or equalising chamber down around a series of coils of pipe, surrounded as described, up over the surface of the water in the vessel, around another outer series of coils, and out at the top of the instrument.

Cold water enters the outer coil at the top, and its temperature is taken by the thermometer shown. It flows down and around the instrument into the last turn of the outer coil which dips into the water, then up the inner coils and into the mixing box. The coils are separated by a non-conducting brattice of two thin brass cylinders, the space between which is packed with cork dust. Condensed water is collected in the large vessel and drips from the side tube. The whole arrangement is very ingenious and fairly convenient. Ninteen of these instruments have been in daily use for more than six years in the official testing places in the County of London without replacement. The most serious defect noticed has been the leakage of water from the coils, mostly at the union joining the inner and outer coil. The official method of using them is given below.

"In order to test the gas for calorific power, the gas shall first pass through a meter and an efficient governor. This may be a balance governor, or a diaphragm governor of a pattern approved by the Gas Referees, and in the latter case the governor may conveniently be placed in the base of the calorimeter. When so placed, a non-conducting sleeve should be introduced into the burner tube to prevent the governor from being unduly warmed by conduction. The gas shall be turned on and lighted, and the form of the two flames observed. If either is out of shape, this must be rectified either by clearing the burner or by substituting another burner. The tap of the calorimeter shall then be so adjusted as to allow the meter hand to make one turn in from 60 to 75 seconds. The water shall be turned on so that when the regular flow through the calorimeter has been established a little may pass the overflow of the funnel and trickle over into the sink. Water must be poured in through one of the holes in the lid until it begins to run out at the condensation outlet. The calorimeter may then be placed upon its base. The measuring vessel carrying the change-over funnel should then be placed in position in the sink so that the outlet water is led into the sink. The hot water outlet tube of the calorimeter should be above but should not touch the change-over funnel. After an interval of not less than 30 minutes the gas examiner, after bringing the reading glasses into position on the thermometers used for measuring the temperature of the inlet and outlet water, shall then make the following observations:— When the meter hand is at 75 he shall read the inlet temperature; when it reaches 100 he shall move the funnel so as to direct the outflow into the measuring vessel and at the same time he shall start the stop-clock or a stop-watch. When the meter hand reaches 25 he shall make the first reading of the outlet temperature. He shall continue to read the outlet temperature at every quarter turn until fifteen readings have been taken. The meter hand will then be at 75. He shall also at every turn of the meter except the last make a reading of the inlet temperature when the meter hand is between 75 and 100. When the meter hand reaches 100 after the last outlet temperature has been read, the gas examiner shall shift the funnel so as to direct the outlet water into the sink again and at the same time stop the clock or watch. The barometer and the thermometers showing the temperatures of the effluent gas, of the air near the calorimeter and of the gas in the meter, shall then be read. The time shown by the stop-clock shall be recorded. The mean of the four readings of the inlet temperature is to be subtracted from the mean of the fifteen readings of the outlet temperature and the difference is to be multiplied by 3 and by the number of litres of water collected, and the product is to be divided by the tabular number. The difference in degrees Centigrade of the temperature of the effluent gas and of the surrounding air shall be taken, and one-sixth of this difference shall be added to the result previously found if the effluent gas is the warmer of the two, or subtracted if the effluent gas is the cooler of the two.* The result is the gross calorific power of the gas in Calories per cubic foot.

"In addition to the observations described, the amount of condensed water resulting from the combustion of the gas shall be

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* A full discussion of this calorimeter and its use will be found in *Calorific Power of Gas*, pp. 226-245 and 246, *et seq.*

measured. For this purpose the condensation water shall be led into a flask not less than twenty minutes after the calorimeter has been placed in position. The amount collected in not less than thirty minutes shall be measured, the time of collection having been accurately noted.

"The number of cubic centimetres collected shall be multiplied by the number of seconds in the time indicated by the stop-clock and by the number 1·86. The number of seconds in the time during which the condensed water was being collected shall be multiplied by the tabular number. The first product shall be divided by the second. The quotient is to be subtracted from the gross calorific power. The difference is the net calorific power in Calories per cubic foot. The gross and net calorific power in British thermal units can be obtained by multiplying the corresponding numbers of Calories by 3·968."

IV. Calculation of Heats of Combustion from Analysis.

If the composition of a gaseous mixture containing combustible constituents is known, its calorific power can be calculated if the heat of combustion of each of these constituents is known.

The total heat of combustion C of a mixture of gases is equal to the sum of the heats produced by the combustion of its constituents. Therefore, if any gas contain constituents a, b, c, d . . . in the proportions q_a, q_b, q_c, q_d . . . respectively, and these gases have, under defined conditions of measurement, calorific values equal respectively to c_a, c_b, c_c, c_d . . . then the value under similar conditions of measurement of

$$C = \Sigma q c = q_a c_a + q_b c_b + q_c c_c + q_d c_d \ \ldots$$

The accuracy of the method depends on the accuracy of (1) the analysis, (2) the values taken for the calorific power of the constituents.

(1) The methods of gas analysis are quite reasonably accurate, so far as they go, but their great weakness lies in the absence of any trustworthy means of determining the nature of the hydrocarbons absorbed by bromine or Nordhausen sulphuric acid. These may include members of the series $C_n H_{2n}$, $C_n H_{2n-2}$ . . . $C_n H_{2n-6}$. A consideration of the heats of combustion of ethylene, propylene, acetylene, and benzene (Table XXXI.) will show that the heating effect of these hydrocarbons in a gas may differ widely according to their nature.

TABLE XXXI.—Calorific Values of Gases at Constant Pressure.

Gas or Vapour.	Calories per Cubic Foot.				(C) B.T.U. per Cubic Foot at 60° F. and 30″. Moist.		(D) Calories per Cubic Metre. Moist.	
	(A) At 0° and 760 mm. Dry.		(B) At 60° F. and 30″. Moist.					
	Gross.	Net.	Gross.	Net.	Gross.	Net.	Gross.	Net.
Methane, .	268	240·5	250	224·3	992	890	8,829	7,921
Ethane, .	468	427·0	436	398	1,730	1,579	15,398	14,056
Ethylene,	421	394	393	367	1,559	1,456	13,879	12,961
Propylene,	622	581	580	542	2,301	2,151	20,483	19,141
Acetylene,	392	378	366	352	1,452	1,397	12,926	12,431
Benzene, .	1,010	969	942	904	3,738	3,587	33,268	31,926
Hydrogen,	86·4	72·8	80·6	67·9	320	269	2,847	2,398
Carbon monoxide,	85·9	85·9	80·1	80·1	318	318	2,829	2,829

Note.—[A × ·9324 = B], {B × 3·968 = C}, (B × 35·316 = D).

The matter has been fully discussed by one of us in another work.* It may be said here that, whereas a consideration of the probable survival of gases after exposure to high temperatures leads to the conclusion that ethylene and benzene, with perhaps traces of acetylene, are the individual substances most likely to be present in, say, coal gas, in any amount, general experience shows that the calorific power of the mixed unsaturated hydrocarbons appears to approximate most closely, as a rule, to that of propylene. We do not suggest that this hydrocarbon is necessarily present in appreciable amount, and we advise that either the values for propylene should be used, or the following, based on the analysis and the determination by direct means of the calorific power of London gas :—

Gross, ... 670 Calories per cubic foot.
Net, ... 600 „ „

We give the following example to illustrate the method of calculating the calorific power of a gas from its composition :—

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* *Calorific Power of Gas,* p. 81.

TABLE XXXII.—Calorific Power of Gas.

	A. Per-centage.	B. Calorific power. Moist gas at 60° and 30″.		$\frac{A \times B}{100}$ = calorific effect.	
		Gross.	Net.	Gross.	Net.
CO_2,	2·5	..	..	..	..
O_2,	·7	..	..	..	..
Unsaturated hydrocarbons,	4·4	670	600	29·5	26·4
CO,	16·5	80·1	80·1	13·2	13·2
CH_4,	23·2	250	224·3	58·0	52·0
H_2,	40·6	80·6	67·9	32·7	27·7
N_2,	12·1	..	..	..	..
	100·0	..	..	133·4	119·3

	Gross.	Net.
Calculated calorific power,	133·4	119·3
Determined calorific power (by Boys' calorimeter),	133·9	121·3

CHAPTER VIII

THE CALORIMETRY OF LIQUID FUEL.

Infrequent Necessity of Calorimetry of Liquid Fuel.—Methods approximate to those for Gases or Solids as the Case may be—Use of Junkers' and Boys' Calorimeters for this Purpose—Liquid Fuel burnt in Bomb Calorimeter.

Infrequent Necessity of Calorimetry of Liquid Fuel.—In a previous chapter we have given several specifications relating to the supply of liquid fuels, such as are used for internal-combustion engines and also for steam-raising purposes. The requisite physical characteristics are scheduled, and in some cases information as to the source from which the oil has been obtained is required.

Assuming that the liquids supplied under any particular specification comply with the requirements, and providing that they are derived from a common source, then the determination of the calorific power cannot be regarded as being as frequently necessary as in the case, say, of coal or other solid fuel in which extraneous matters in varying amounts are present. Hydrocarbon oils are, practically, the only liquid fuels used, and, moreover, for specific purposes only fairly definite fractions of these are required.

Now, by far the greater portion of Pennsylvanian oil, commonly known as American, consists of what are known as the paraffin hydrocarbons, having the general formula $C_n H_{2n+2}$. The lowest member of the series is methane or Marsh gas, CH_4, which is gaseous at ordinary temperatures, and the higher members include liquids of high boiling point and solid hydrocarbons, such as $C_{30}H_{62}$. Between these extremes we have a great number of hydrocarbons which are commercially separated into groups, not into individuals, by fractional distillation. The fractions obtained are essentially mixtures of hydrocarbons, of approximately definite range of specific gravity and boiling point. If we calculate the heats of combustion of two of these individual hydrocarbons of widely differing boiling points, the reason for the statement as to the infrequent necessity of determining the calorific power of supplies delivered to and complying with specified requirements will be manifest. We will compare the hydrocarbon hexane, C_6H_{14}, which is present to a great extent in petroleum spirit, the lightest fraction obtained in the distillation of the crude petroleum, with hexadecane, $C_{16}H_{34}$, one of the higher boiling-point liquids contained in the burning oil fraction.

The boiling point of the former is 69° C., whereas that of the latter is 280° C.

The percentage compositions are :—

	Carbon.	Hydrogen.
Hexane, ...	83·72	16·28
Hexadecane, ...	84·95	15·05

By multiplying the respective amounts of carbon and hydrogen by the heats of combustion of these two elements we obtain the heat evolved by burning 1 gramme of each of these compounds. The figures thus obtained are irrespective of the heat of formation (which is very small) of these two substances, but they are practically correct.

$$\text{Hexane, . . } \left.\begin{array}{c}(0{\cdot}8372 \times \ \ 8{,}140)\\ +\\ (0{\cdot}1628 \times 34{,}500)\end{array}\right\} = 12{,}432 \text{ Calories per gramme.}$$

$$\text{Hexadecane, . } \left.\begin{array}{c}(0{\cdot}8495 \times \ \ 8{,}140)\\ +\\ (0{\cdot}1505 \times 34{,}500)\end{array}\right\} = 12{,}107 \quad \text{,,} \quad \text{,,}$$

The difference, it will be noticed, is 325 Calories on 12,432—*i.e.*, about 2·6 per cent.—and this on two widely separated members of the "paraffin" series.

Similarly, between what are probably the highest and lowest members of the petroleum spirit fraction (such as "petrol"), the difference would not exceed 1·5 per cent.

If the difference between the extreme members of any one fraction is so small, it follows that the differences in the calorific values of similar fractions, which, as previously stated, are *mixtures* of several hydrocarbons, will be still less pronounced.

This statement is confirmed by the results obtained from the examination of a number of samples of these light petroleum fractions by Bertram Blount. They were embodied in a paper read before the Incorporated Institution of Automobile Engineers (March, 1909). The figures obtained by him are as follows :—

TABLE XXXIII.—Calorific Power of Light Petroleum.

Specific Gravity.	Calorific Value.	
	A. Calories per kilo.	B. Calories per litre.
0·739,	11,162 (−76)	8,249
0·717,	11,252 (+14)	8,068
0·717,	11,229 (− 9)	8,051
0·715,	11,260 (+22)	8,017
0·700,	11,302 (+64)	7,911
0·718,	11,200 (−38)	8,042
0·717,	11,187 (−51)	8,021
0·715,	11,267 (+29)	8,056
0·705,	11,289 (+51)	7,959
0·705,	11,232 (− 6)	7,919

It will be noticed that the greatest difference between any two results in column A is 140 Calories; the average of the ten results being 11,238 Calories per kilo.; the variation above or below the average figure is given in brackets. The figures in column B differ considerably, but this is obviously due to the difference in specific gravity of the different samples, and in discussing the results obtained, Blount remarked "that it is obviously more advantageous to purchase petrol having a high specific gravity, provided that it can be burnt efficiently, so long as the system of selling by volume is adhered to."

It must not, however, be inferred from the foregoing that we do not advocate the determination of the calorific power of liquid fuel; our point is that when dealing with definite fractions of oils of known origin the necessity of such determination is not as essential as in those cases which arise when dealing with liquids of unknown origin, or in those which contain varying quantities of cyclo-paraffins and olefines. These latter bodies contain less hydrogen than the "paraffins," and in consequence have lower calorific values.

Liquid Fuel burnt in Bomb Calorimeter.—The most suitable apparatus for the determination of the calorific power of liquid fuels is, without doubt, a calorimeter of the bomb type, as it may be used for *all* of the various liquids used as fuel, ranging from the highly volatile petroleum to the heavy viscous petroleum residuum.

With regard to the volatile liquids, it is not a simple matter to weigh a definite quantity and transfer it without loss (due to evaporation) to the combustion chamber. This difficulty, so far as the bomb calorimeter is concerned, has been overcome by the use of a deepish cup, the top of which is provided with a celluloid cap, which is contracted at the top so as to form a narrow mouth. This device, due to Berthelot, was used by Blount in the work previously referred to, and was found to moderate the combustion of the petrol, thus ensuring complete combustion and avoiding the violent explosions which he had previously experienced.

The calorific value of the celluloid cap is known and deducted from the result obtained.

With the other classes of liquid fuel no special precautions are necessary, and in all cases the mode of procedure is similar to that described in the next chapter when dealing with the calorimetry of solid fuel. The other methods of determining the calorific value of this class of bodies are :—

(*a*) If the fuel is of a volatile character an air gas may be prepared and burnt in the gas burner of a flow calorimeter or a still-water calorimeter, such as is used for gases, or the liquid may be burned from a lamp and used with the same calorimeter.

(*b*) If the fuel is of a non-volatile character, it may be mixed with kiesel-guhr or other absorbent material, and then treated as a solid fuel.

The former method obviously can only be strictly accurate when dealing with chemically pure substances: with liquids consisting of mixtures it is possible that fractional volatilisation would occur, and the results would consequently be more or less inaccurate, according to the dissimilarity of the different compounds present in the fuel.

Julius Thomsen conducted the whole of his work on the calorific power of pure gases, liquids, and solids by burning the different substances in an atmosphere of oxygen, the calorimeter being of the still-water type. He deduced the weight of fuel burned by collecting the products of combustion and determining the amounts of carbon and hydrogen therein (usually only the carbon).

For all ordinary work such a method would be too protracted and, as previously mentioned, only chemically pure substances could be dealt with.

Prof. Watson has determined the calorific values of light petroleum by vapourising the spirit and burning the resulting gas in the Boys calorimeter.

The method is described in the *Proceedings of the Incorporated Institution of Automobile Engineers,* session 1908-9, vol. iii., p. 429.

The petrol is allowed to flow from a bulb of known capacity through a capillary tube surrounded by a water jacket; from thence it drops from a jet on to a number of discs of wire gauze arranged in a vertical tube, which is surrounded by a steam jacket. A steady current of air passes up this tube, and is so regulated that the petrol is completely vapourised; it is then carried through a side tube connected to a Bunsen burner, in which combustion takes place; the amount of heat evolved is measured by noting the volume of water passing through the calorimeter and the increase of temperature in a given time.

The following instructions for the determination of the calorific power of *light* and *heavy* liquid fuels are issued with Darling's calorimeter :—

" **For Light Liquid Fuels.**—1. Prepare a wick of asbestos fibre for the lamp. This wick should fit the nozzle tightly, and be of sufficient length to reach the bottom of the lamp. For petrols, the smallest nozzle must be used; for petroleum, alcohol, and the heavier oils generally, the wider nozzle should be employed.

" 2. Place about 1 c.c. of the liquid in the lamp, screw on the cap, and weigh accurately. Then fix the lamp in the clips, and place the glass cover in position, taking great care to ensure a tight joint on the rubber ring. An extra ring may be used to advantage.

" 3. Fill the cylinder with water to the 1,400 c.c. mark, and then, by means of a pipette, transfer sufficient of this water to the interior of the bell-jar to immerse the lamp to about three-fourths of its height.

" 4. Turn on a stream of oxygen, and allow it to bubble from the delivery tube through water. Adjust the rate of flow so that the bubbles arising just cease to be discontinuous as judged by the eye. This rate of flow will generally prove satisfactory for burning liquid fuels. Now note the temperature of the water.

" 5. Allow some of the oxygen to enter the bell-jar. Then ignite the wick by lowering a lighted match, fastened to a rod, into the interior. Quickly insert the oxygen tube, and immerse the calorimeter in the water. Allow the combustion to proceed until the lamp is extinguished, and then lessen the oxygen supply until bubbles just escape from the perforated plate below. Now raise the calorimeter, and slacken two of the screws, when the pressure of the oxygen will force the water from the bell-jar into the cylinder. Tighten the screws, and again immerse the calorimeter, and note the steady temperature attained by the thermometer.

"6. Remove the calorimeter, take off the bell-jar, carefully dry the lamp externally with blotting paper, and weigh again. The loss in weight gives the amount of fuel burnt. The calorific value, as before, is obtained from the equation—

$$\text{Calorific value} = \frac{(\text{weight of water} + \text{water equivalent}) \times \text{rise in temperature}}{\text{Weight of fuel burnt}}.$$

"*Precautions.*—(*a*) If a secure joint is not made between the bell-jar and the rubber ring, the enclosed water is driven out by the pressure of the oxygen. The heat generated then causes the fuel to boil, and an explosion may follow. If the inner water be observed to be leaking, the experiment should be stopped at once and repeated more carefully.

"(*b*) When the flame is extinguished on immersing the calorimeter in the water, the cause is almost invariably a deficient supply of oxygen, which accordingly should be increased.

"(*c*) Care should be taken, after the combustion, to prevent the detachment of any portion of the asbestos wick, which becomes brittle owing to the heat.

"(*d*) If the fuel be so heavy as to fail to burn continuously from an asbestos wick, it should be dealt with as described below.

"**For Heavy Liquid Fuels.**—1. Weigh out about 0·75 gramme of the liquid into the nickel crucible. This is best done by first weighing the crucible, and then adding roughly 1 c.c. of the liquid from a burette or pipette, and then weighing again.

"2. Add 1·5 grammes of ignited kaolin or calcined alumina to the liquid in the crucible, place in position, establish a steady stream of oxygen, and ignite electrically. If the sulphur ignition be used turn on the oxygen to the required amount before inserting the oxygen tube in the bell-jar. The oxygen must be kept in excess.

"*Special Note.*—The amount of kaolin or calcined alumina stated will generally suffice to secure smokeless and tranquil burning. Should smoking ensue, raise the oxygen tube, as in the case of smoky solid fuels, and depress it gradually during the progress of the combustion.

"The patent copper bell-jar will be found most suitable for heavy liquid fuels, as the great heat generated on combustion may cause a glass bell-jar to crack.

"3. The calorific value and evaporative power may be calculated in the same manner as for solid fuels."

The results obtained are probably as satisfactory as can be expected with a calorimeter of this type ; the difficulty in obtaining complete combustion of solids in this and similar calorimeters working with low-pressure oxygen is well known, and these difficulties, especially when working with very volatile substances, are increased, owing to the greater tendency of the volatile hydrocarbons to escape complete oxidation.

Berthelot worked with a calorimeter which may be regarded as typical of all subsequent low-pressure oxygen instruments, and he finally discarded it in favour of the bomb calorimeter.

His reasons for discarding the low-pressure type of apparatus are given in his *Traité Pratique de Calorimetrie Chimique*, 1905. "This and similar methods for the determination of the heat of combustion of carbon, hydrocarbon gases, and organic compounds leaves much to be desired. In practice, one encounters serious difficulties, due to two causes :—

"(*a*) The combustion in a current of oxygen requires a fairly long time, and thus necessitates a large correction (for radiation, etc.). (*b*) Above all, *the combustion is never complete*, and a certain amount of carbon monoxide and unburnt hydrocarbons are produced. To this last circumstance serious errors in the early determinations of the heats of combustion of carbon are attributed."

Rosenhain's calorimeter, which is described in the next chapter, may be used for heavy liquid fuels, a known weight of the oil being poured on to an absorbent pellet, which is then burnt in the combustion chamber in the same way as if dealing with solid fuel. A useful innovation in this case is the preparation of the "absorbent" from a substance which is completely combustible, and the calorific value of which is given with the pellets supplied. This value would, of course, be deducted from the results obtained.

This method is obviously only applicable in those cases in which the liquid is practically non-volatile at ordinary working temperatures, and the results obtained, even in these cases, cannot be regarded as more than fairly accurate.

CHAPTER IX.

CALORIMETRY OF SOLID FUEL.

Calculation of Calorific Power—Dulong's Formula—Constam's Formula for Coke—Calorimetric Apparatus. **I. Oxidising Mixture Calorimeters**—Lewis Thompson's, Parr's, Roland Wild's. **II. Low-Pressure Oxygen Calorimeters**—William Thomson's, Darling's, Rosenhain's, Fischer's. **III. High-Pressure Oxygen (Bomb) Calorimeters**—Berthelot's, Mahler's, Mahler-Kröcker, Sarco, Hempel's—Method of Using Corrections for Sulphuric and Nitric Acid in Bomb—Féry's Thermo-electric Bomb—Gross and Net Values—Seyler's and Lucion's Formulæ—Limits of Accuracy—Conclusion.

Calculation of Calorific Power.—It has been shown in a previous chapter (p. 213), that it is possible to calculate the calorific value of a gaseous mixture provided that its percentage composition is known. The only real difficulty (apart from the experimental errors incidental in gas analysis) arises from the fact that it is not possible to state exactly what calorific value is to be assigned to the unsaturated hydrocarbons present. As these, however, are usually present to a very small extent, and as it has been found possible to arrive at a good working figure, based upon experience, for their calorific value, the results usually obtained agree very well with those obtained by the direct determination of the heating value.

Obviously this method of procedure would be adopted only in those cases in which the amount of gas at our disposal was very small, and a direct method could, therefore, not be used. The important fact to remember is that we know the amounts of definite chemical compounds and elements contained in the gas, and also their respective heats of combustion.

Dulong's Formula.—Dulong proposed a formula for the calculation of the calorific power of coal, which was based upon the *ultimate* analysis of the fuel, and the heats of combustion of the elements, carbon, hydrogen, and sulphur.

The formula proposed is—

$$8{,}080\ \mathrm{C} + 34{,}460\left(\mathrm{H} - \frac{\mathrm{O}}{8}\right) + 2{,}250\ \mathrm{S},$$

where C = amount of carbon, H = hydrogen, O = oxygen, S = sulphur.

It will be at once evident that there is no scientific basis underlying the proposed formula, since it disregards the heat of formation of the proximate constituents of coal, and from it one would be justified in regarding coal as a mere mixture of different weights of free carbon and sulphur with a certain amount of free hydrogen, water, and nitrogen.

The difference between this method of the calculation of heat of combustion and that of the gases previously referred to is obviously pronounced, as in the latter case we know the *state of combination* in which the different elements are present.

Again, the amount of oxygen in coal is obtained as a difference-figure, and we have already shown how all the errors incidental to the ultimate analysis are thrown on to the oxygen; consequently, this figure can hardly be regarded as a true factor when used in the formula quoted, and especially as it is unwarrantably assumed to be present only in combination with hydrogen as water. Workers on the calorific power of coal have usually compared their results with those calculated from the formula given, and in most cases have endeavoured to modify the formula to suit their figures.

Mahler recognised that the ordinary Dulong formula was unsatisfactory when the oxygen and nitrogen are high, and substituted

$$\mathrm{Q} = \frac{1}{100}\left[8{,}140\,\mathrm{C} + 34{,}500\,\mathrm{H} - 3{,}000\,(\mathrm{O} + \mathrm{N})\right].$$

Gray and Robertson* and Brame and Cowan† used the following expression:—

$$\mathrm{C.V.} = \frac{\left[8{,}140\ \mathrm{C} + 34{,}500\left(\mathrm{H} - \frac{(\mathrm{O}+\mathrm{N}) - 1}{8}\right) + 2{,}220\ \mathrm{S}\right]}{100}.$$

It will be seen that the attempts to reconcile determined values with those calculated from Dulong's formula have proved futile,

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* *Journ. Soc. Chem. Ind.*, 1904, p. 704.

† *Journ. Soc. Chem. Ind.*, 1903, p. 1230.

and athough with some classes of coal the latter course has proved fairly satisfactory, yet, in those cases in which the amount of oxygen is large, the results are untrustworthy. It must be borne in mind, however, that until the advent of the bomb calorimeter no really reliable calorimetric results were available for solid fuel, and the errors of the calculated results were possibly not seriously greater than those of the values determined with the older forms of calorimeter.

Brame and Cowan * remark that "there does not at present appear to be that close agreement between calculated and determined values in certain forms of bomb calorimeter which some writers have claimed. That a fairly close agreement exists with a large number of coals may be granted, but exceptional cases arise, and these being always likely to occur, make calculated results of doubtful value."

Gray and Robertson conclude their remarks on this point as follows :—"But it is evident that the method of calculation from analytical results only gives approximate values, and that *it should be only employed in cases where a direct determination is not possible.*"

Another important point is that the time necessary for a complete ultimate analysis of a coal, which must be made before the figure for calorific value can be calculated, is at least five or six hours, whereas with a bomb calorimeter it is possible to make a determination of the calorific value within an hour, or including the estimation of the sulphuric and nitric acids produced during the combustion, an hour and a-half. Thus, not only are the results of direct calorimetric experiment more trustworthy, but they are obtained in a much shorter time. Of course, it may be urged that the ultimate analysis would probably be made in any case, and that the calculation of the calorific power would then be only a small matter ; this would be true in those cases where the ultimate analysis was necessary, but under ordinary circumstances a proximate analysis of the fuel, in conjunction with a determination of the calorific power, is considered as giving sufficient information.

We may conclude our remarks on this question of calculation of calorific power from the results of ultimate analysis by giving the "determined" values of methane, CH_4.

The figures obtained by Berthelot and Julius Thomsen are respectively 213·5 and 211·9 great Calories per gramme molecule,

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* *Loc. cit.*

whereas the calculated value from the heats of combustion of carbon and hydrogen would be 235·0 Calories.

The difference between the experimental and calculated values is reasonably attributable to the fact that in the formation of a gramme molecule of methane from its elements about 22 *great Calories are evolved*, and, consequently, before the combustion of the gas into CO_2 and H_2O can take place *these* 22 *Calories are absorbed* in breaking down the compound itself.

If these differences are encountered when dealing with comparatively simple combinations of carbon and hydrogen, it is obvious that a far more unsatisfactory state of affairs prevails when 5 (or more) per cent. of oxygen is present as well.

Constam's Formula for Coke.—This, unlike Dulong's formula, is based on fairly sound premises, for, if the coke has been properly prepared, the only combustible elements present in appreciable amount will be carbon and sulphur. As it is necessary to determine the sulphur, in order to apply the necessary correction to the calculated result, and as, moreover, this is best accomplished in a bomb calorimeter, it would be more satisfactory to determine the calorific value directly, on the portion in which the sulphur is to be determined. It would only delay the sulphuride determination by a few minutes, and at the same time would give one the satisfaction of a *directly determined* value for the calorific power. If, however, a calorimeter is not available, the formula may be used :—1 gramme of the finely powdered coke is taken and heated for two hours in a platinum crucible at 110° C. The loss of weight represents the moisture in the coke. The dried portion is heated to incandescence in the crucible until the combustible matter is burnt off, and the residue is the ash in the coke. If, for instance, the moisture is 1 per cent. and the ash is 9 per cent., the coke may be considered good. It contains 90 per cent. of combustible matter.

It has been established that the gross calorific power of all cokes produced under the uniform conditions of the experimental gas plant used by Constam is practically constant at about 8,000 *Calories per kilogramme* = (14,400 *B.Th.U. per lb.*).

Hence, by multiplying the proportion of combustible matter by its constant calorific value in the sample $\frac{90}{100} \times 14{,}400 =$ 12,960 B.Th.U. per lb. we obtain the gross calorific power of the coke within 1 per cent. of the truth. A deduction of 90 B.Th.U. would give the net calorific power. In using this method it must be borne in mind that the coke must be true coke—*i.e.*, not be imperfectly carbonised—and that a high percentage of sulphur in the coke would vitiate the result, since 1 per cent. of sulphur in the dry ash free coke means a reduction in calorific value of rather over 100 B.Th.U. per lb.

Calorimetric Apparatus.—The apparatus used for the determination of the calorific power of solid (and liquid) fuels is less complicated than that required when dealing with gases, inasmuch as we are dealing with substances of which the mass may be directly determined on the balance.

The calorimeters employed are all of the still-water type, and the other apparatus required includes a sensitive balance for the weighing of the fuel and a larger and less sensitive one weighing up to about 5 kilos, and sensitive to about 0·5 gramme.

For the electrical ignition of the fuel we have found small accumulators giving a current of 4 amperes at 2 volts extremely satisfactory. A word of warning may, perhaps, be of use here; we do not advise dependence on batteries of dry cells for electrical ignition; on several occasions they have given out quite suddenly, and nothing is more annoying than to have to take the apparatus to pieces suspecting a miss-fire and to find eventually that the battery is exhausted. This relates particularly to the bomb type of calorimeter, in which it is, of course, quite impossible to see what is occurring when once the cover is bolted on or screwed down.

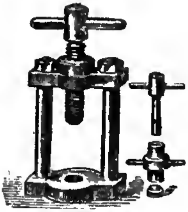

Fig. 49.—Press for fuel.

Another piece of apparatus often used when dealing with solid fuels is a small press (Fig. 49), which is employed for compressing the powdered fuel into a pellet of approximately 1 gramme weight. Although these are used to a fairly large extent, we have not found any difficulty in burning the fuels in the powdered form, and consequently have never troubled about having one.

The types of calorimeter used for solids are three in number, namely:—

(1) Those in which the powdered fuel is intimately mixed with a solid or mixture of solids containing a large amount of readily available oxygen, which, once the combustion is started, is sufficient to supply the necessary oxygen for the complete combustion of the fuel.

(2) Those in which the fuel is burned in a stream of oxygen gas at constant pressure.

(3) Those in which the fuel is burned in a large excess of oxygen gas at a high pressure, and at constant volume.

I. **Oxidising Mixture Calorimeters.**—In the first division we have three calorimeters—Lewis Thompson's, Parr's, and Rowland Wild's.

Lewis Thompson's calorimeter is probably the earliest practicable instrument to have been used seriously for coal testing, and we are credibly informed that until a few years ago it was still used to a very great extent.

The apparatus consists of a *glass* cylindrical vessel *A*, which is the calorimeter proper. On it are two etched lines, the upper one being marked 2,000 c.c., the lower 1,934 c.c.

The "condenser" *B* consists of a copper cylinder open at the lower end, with a number of holes punched round the lower edge to allow the products of combustion to escape. A copper or brass tube is fitted into the otherwise closed end of the cylinder, and is provided with a tap *b*. The mixture of the fuel and "oxygen-containing substance" is introduced into a furnace tube *C*, which in turn is fixed into a metal stand *D* provided with spring clips *d*. The condenser *B* is forced over the clips *d*, which are sufficiently stiff to allow the whole to be lifted by means of the tube of the condenser and lowered into *A*. A thermometer usually graduated in tenths of a degree Fahrenheit is placed in *A*. The bottom flange of the stand *D* is perforated so that on raising and lowering the metal portion by means of the condenser the contents of *A* are thoroughly mixed.

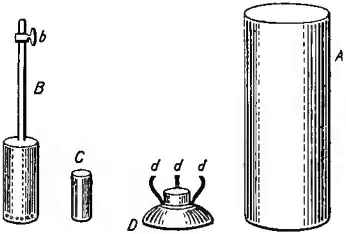

Fig. 50.—Lewis Thompson's calorimeter.

To determine the calorific power of a fuel by means of this apparatus the coal is ground in a mortar until the whole of the sample will pass through a sieve of 60 meshes to the linear inch. The finely powdered coal is then transferred to a drying oven and, when dry, is transferred to a stoppered weighing tube.

Two grammes of the dried fuel are intimately mixed with from 11 to 13 times its weight of a mixture of 3 parts of potassium chlorate and 1 of potassium nitrate, prepared by grinding and sifting.

The mixing is best conducted on a sheet of glazed paper, by means of a flexible steel spatula, and, when completed, the mixture is transferred to a furnace tube by means of the spatula. After each portion of the mixture has been introduced it is gently rammed down ; we have found that the most suitable " rammer " is a thick-walled test tube which just fits the furnace tube. When all has been transferred, a piece of touch cotton, about 1 inch long, is inserted into the mixture, to a depth of ½ inch, and the surface of the latter is loosely raked round the fuse, and the tube is then fitted into the socket of the stand *D*.

The touch cotton is prepared by soaking some wick, such as is used for ordinary spirit lamps, in a solution of potassium nitrate, and then drying in the oven. About an inch of the fuse should be ignited, and if it burn violently, the remaining portion should be rubbed between the hands until another portion 1 inch long is found to burn out in about 5 to 10 seconds. This point is essential, as if the fuse is too " quick " the combustion will commence before sufficient time has elapsed for the transference of the condenser, etc., to the calorimeter. The calorimeter vessel is now filled with water to the containing-mark, 2,000 c.c. or 1,934 c.c., and the temperature adjusted so that it is from 4° to 5° F. below that of the room ; when it appears to be constant the temperature is noted, the exposed fuse in the furnace tube is lighted, the condenser *with the tap closed* is quickly forced over the spring clip, and the whole apparatus held in the hand by means of the pipe is placed in the calorimeter vessel with the base just above the water. As soon as the combustion is heard to start, the whole is immediately submerged ; the thermometer is placed in the calorimeter ; and the progress of the combustion is noted ; it should proceed quietly and regularly, and should not occupy *less* than a minute. By using the maximum weight of oxidising mixture and carefully packing the tube we have not experienced any difficulties, such as explosive combustions, but this was only when dealing with a class of coal for which this apparatus seems to be peculiarly adaptable. As soon as the combustion is complete, the inner apparatus is raised and lowered several times, and the tap is opened ; this allows the water to enter the condenser, and the mixing of the water is continued by alternately raising and lowering the metal portion of the apparatus until the temperature no longer rises.

The rise of temperature increased by 10 per cent. and multiplied by 1,000 equals British thermal units per lb. of coal if the vessel has been filled to the 2,000 c.c. mark, or the number of pounds of water evaporated from and at 212° F. by 1 lb. of coal if the 1,934 mark has been used.

We have described this apparatus and the method of using it fully, as we have had considerable experience with it. By making a correction for the amount of unburnt fuel, the results obtained *in the case of bituminous coals* are surprisingly good, but with other coals they are of little or no value. The method of correcting for unburnt fuel, is to acidify the contents of the calorimeter, after having dissolved all the saline matters present in the furnace tube and condenser, filter, and determine (by weighing on a filter and subsequent ignition) the amount of carbon in the dried residue. This, in the case of bituminous coals, we found to be very small indeed, but with anthracites especially we always found a very large amount of unburnt fuel. In making the correction for unburnt fuel it is not known if it consists of carbon or merely unburnt coal, but it is, perhaps, best to assume that it is carbon. This determination of unburnt fuel is a tedious business, and one that nullifies any claim that the method is convenient and expeditious.

Our experience is that the method gives fairly good results, both as regards agreement among themselves and when compared with the results obtained from the bomb calorimeter, but *only in the case of highly bituminous coals.* Brame and Cowan and Gray and Robertson arrived at the same conclusion; the former authors remark "that the estimation of the unburnt coal is so tedious an operation, and one which would be seldom carried out in practice, that most observers would rely on the uncorrected figure, and this would be so far from the truth, except with a highly bituminous coal, as to be quite valueless."

Gray and Robertson say—"At best the method may be taken to give a very rough indication of the heating values of bituminous coals. The directly determined numbers in such a case may deviate from the absolute heating values by as much as 8 per cent."

The errors, which are at once obvious in this apparatus, are losses due to unburnt fuel, losses due to the combustion proceeding too rapidly to enable the products to be deprived of all their sensible heat, and the heat changes accompanying the decomposition of the oxidising mixture. In addition, we have the unsatisfactory glass containing vessel, and the irregular radiation from an apparatus used without any protection from external influences. It is probable that most of these were assumed to be allowed for in the 10 per cent. correction, but one can only regard it as being of service where strict accuracy is not essential, or where difficulty is experienced in obtaining compressed oxygen.

Parr's Calorimeter.—This consists (Fig. 51) of a strong metal combustion chamber, the ends of which are screwed on, leather washers being provided to ensure the joints being gas-tight. A known weight of the finely powdered and, if necessary, previously dried fuel is intimately mixed with 10 grammes of sodium peroxide in the combustion chamber, which is then placed in a metal calorimeter vessel containing 2 litres of water. This is placed inside a wooden vessel, which is in turn placed inside a second similar wooden vessel.

The upper portion of the combustion chamber consists of a tube, inside of which is a narrower one notched on one side and continued downwards to a conical valve, by means of which the inlet to the combustion chamber may be closed or opened at will by pressure of a spring attachment. A pulley is mounted on the top of this tube, and is connected to the motive power during a determination. The bottom of the combustion chamber rests on a conical pivot, which forms a part of a small inner vessel, which surrounds the lower part of the combustion chamber. Four small propeller blades, which are affixed to the latter by means of spring clamps, ensure a rapid circulation of water through the inner vessel when the motor is started, and thorough mixing of the water in the calorimeter vessel is obtained. The ignition of the mixture is effected by dropping a piece of red-hot iron into the tube and sharply depressing the head of the same, so that the valve is momentarily opened to allow the iron to enter the combustion chamber.

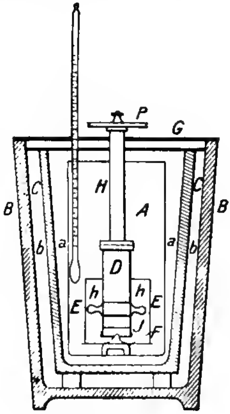

Fig. 51.—Parr's calorimeter.

Lunge * recommends the following method for making a determination :—

The coal to be tested should be powdered, so that it will pass through a wire sieve of 0·3 mm. ; in the case of hard coals and

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* *Z. angew. Chem.*, 1901, vol. xiv., pp. 794 and 1270; 1903, vol. xvi., p. 911; 1905, vol. xviii., p. 1249.

anthracite a more finely divided sample should be used, which may be obtained by placing a piece of bolting cloth under the sieve.

Lignite must be previously dried for about one hour at a temperature of 105° to 110° C. Exactly 1 gramme of this substance is weighed out and shaken into the combustion chamber previously charged with 10 grammes of sodium peroxide (passed through a sieve of 1 mm. mesh), after which the vessel is closed and shaken for one or two minutes. Bituminous coals do not require previous drying unless the moisture exceeds 2 to 2½ per cent. In the case of coal exactly 0·5 gramme is taken, and to this is added exactly 0·5 gramme of finely powdered pure tartaric acid; this mixture is then added to the 10 grammes of peroxide as usual.

After the combustion chamber, with its attachments, has been placed in position, the cover is placed on the apparatus in the calorimeter vessel previously filled with 2,000 grammes of water, the pulley is attached, and a speed of about 150 revolutions per minute is maintained until the reading of the thermometer is constant. This usually takes about three minutes, the temperature is noted, and the motor is kept running at the same speed until the determination is concluded. A piece of red-hot iron, weighing about 0·4 gramme, is then introduced, and the rise of the thermometer is noted until the maximum temperature is attained. This is said to remain constant for about five minutes, and is noted.

The apparatus is now dismantled, the combustion chamber is opened, and the contents dissolved by means of warm water. Should any unburnt fuel be observed, the results are worthless. In a calorimeter the total water value of which is 2123·5 grammes, 72·5 per cent. of the heat produced is regarded as due to the combustion of the fuel, and 27·5 per cent. to the reaction of the products of combustion with the oxidising reagents.

When, for example, 1 gramme of lignite is burned, (the weight of water + the water equivalent of the apparatus) × rise of temperature does not give the heating value of the fuel. It is necessary to deduct 0·015° C. (the supposed equivalent of the heat introduced by the iron wire) from the recorded increase of temperature, and to multiply the corrected figure thus obtained by 0·725 of the total water value.

When dealing with coals an additional deduction for the heat of combustion of the tartaric acid has to be made.

This method has obvious defects, and although it is claimed

PLATE VII.

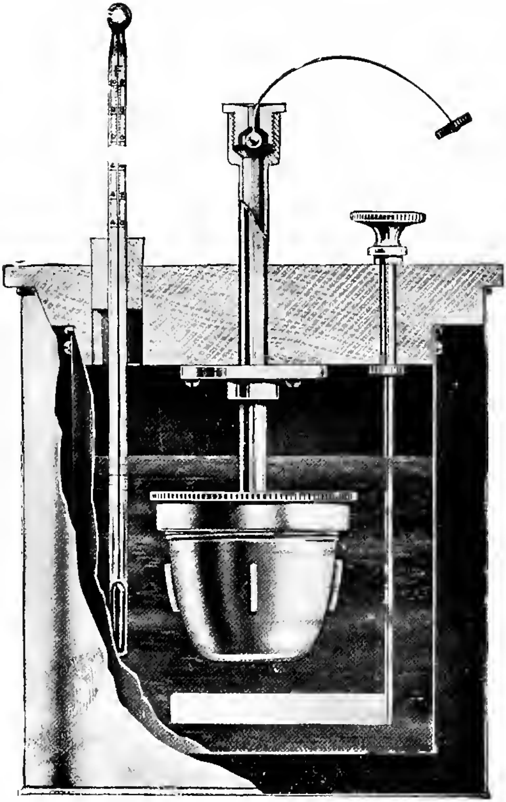

Fig. 52.—Roland Wild's Calorimeter.

that it is more convenient, simpler in manipulation, and cheaper than methods involving the use of a bomb calorimeter, we are of opinion that the results obtained cannot be regarded with the same confidence as those obtained by the latter instrument.

The uncertainty as to the completeness of the combustion and the empirical determination for each instrument of the thermal effect produced by the interaction of the water and carbon dioxide with the peroxide, as well as the possible changes in this reagent due to absorption of moisture, are very disturbing factors, and difficulties, which are ever liable to occur, can only be partially eliminated by repeated blank experiments.

Lunge and Offerhaus (as also Lunge and Grossmann) have specially investigated these points, and the latter conclude that the method is unreliable for coals having a calorific value less than 7,500 calories per gramme; for coals having a higher calorific value the method is of practical value.

Langbein * discards Parr's process as altogether unreliable, but this conclusion, it is stated, is not justified.

Roland Wild's calorimeter is a modification of that by Parr. Fig. 52 sufficiently indicates its construction. It is used to some extent in this country, and workers with it inform us that they consider that results obtained with it are sufficiently near the truth to be of considerable use, at any rate for comparative purposes. We are indebted to the makers for the figure given.

II. Low-Pressure Oxygen Calorimeters.—The calorimeters in which the fuel is burnt in a current of low-pressure oxygen are, in principle, similar to those used by Julius Thomsen, and at one time by M. Berthelot, although the latter worker subsequently discarded this type of apparatus for his "bomb." There is no doubt that the general applicability of these pieces of apparatus for fuel calorimetry renders them of more value than the Lewis Thompson form, and they have distinct advantages over the somewhat "pyrotechnic" calorimeters generally. There is no necessity of making the enormous empirical corrections which we have already indicated when describing these calorimeters.

On the other hand, Berthelot's considered opinion of these low-pressure oxygen calorimeters is, on the whole, confirmed by those who have had occasion to use them, and those responsible for their introduction do not claim that they give results of absolute accuracy; but, and we think justifiably, they maintain that it

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* *Z. angew. Chem.*, vol. xvi., p. 911, 1903.

is possible by the use of these calorimeters to obtain comparative figures which enable one to pronounce an opinion as to the variation or otherwise of regular supplies of fuel.

When one considers that such forms of calorimeters are relatively inexpensive when compared with the bomb type of calorimeter, it must be granted that they serve a useful purpose, and there is no doubt that when *standardised* against a *fuel of known calorific value* the differences between the results subsequently obtained and those given by calorimeters of the highest class are very considerably reduced.

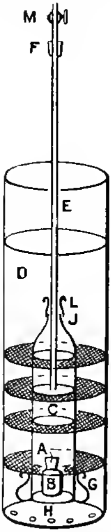

Fig. 53.—William Thomson's calorimeter.

William Thomson's Calorimeter (Fig. 53).—The calorimeter ascribed to, and known as the, William Thomson was fully described in the *Journ. Soc. Chem. Ind.*, p. 581, 1886, from which the following description is taken :—

"It consists of a large glass beaker *D*, which is the calorimeter vessel ; during a determination this is surrounded by a thin polished metal vessel with an opening cut down the side and fitted with a glass window, so that the progress of the combustion may be observed.

"The fuel is burned in a platinum crucible, which is placed on a clay support *B* affixed to a stand *H*, which is fitted with spring clips *G*. An inverted glass tube *C*, 6 inches long by $1\frac{1}{2}$ inches diameter, forms the combustion chamber and fits tightly inside the clips *G*. The upper end is attached by means of a small piece of india-rubber tubing *L* to a copper tube *E*, about $\frac{1}{4}$ inch internal diameter. The rubber connection is arranged so that the brass tube may be readily pushed down into the bell jar as required. The tube *E* is fitted with a tap at *M*, and is connected with the oxygen supply.

"Four circular brass wire gauze rings *K* are attached to the tube *C*, in order to break up the bubbles of gas produced during combustion, and thus more effectually to rob them of their sensible heat.

"The following details are given as to the method of conducting a determination :—

"One gramme of the fuel is weighed into the crucible, which is then placed on the clay support.

"The calorimeter vessel is filled with 2,000 c.c. of water which has been allowed to stand in the room, in which the determination is to be made, sufficiently long to be practically of the same temperature as the air.

"The temperature of the water is noted, and the oxygen supply tube is connected with the gas bottle, the tap *M* being closed; the tube is drawn up so that it is at the top end of *C*, the coal is ignited by means of a piece of fuse, similar to that used with the Lewis Thompson calorimeter; immediately after lighting the fuse, the tube *C* is pressed home, and the whole lowered into the calorimeter. At the same time, the tap *M* is slowly opened, thus admitting oxygen into the apparatus.

"The tube *E* is kept in the upper part of *C* until all the volatile hydrocarbons have been consumed, and is then pushed down until it is immediately over the crucible, to complete the combustion of the glowing coke. A slight rotatory movement of the tube is advised at this stage.

"When the experiment is completed the taps are turned off and the oxygen supply disconnected. The tap *M* is then opened gradually to allow the water to enter the bell. The combustion apparatus is raised and lowered until the water is thoroughly mixed, then withdrawn, and the temperature again taken. For the sake of the subsequent cooling correction the time required for the determination (three to five minutes) is noted.

"All the glass, copper, mercury, iron, brass, etc., connected with the calorimeter, are weighed; and from their specific heats their equivalent in water is calculated.

"The oxygen employed may be measured, and from its specific heat the quantity of heat carried off may be calculated. The specific heat of oxygen being 0·2160 and of carbonic acid 0·2163, and the weight of oxygen used in each experiment being about 8 or 10 grammes, the correction for the heat thus carried off, especially as the total rise of temperature in each experiment does not exceed from 6° to 8° F., is very small. The mean temperature of the gases passing away from the water for each experiment would not exceed 3° or 4° of a rise.* The water converted into vapour may also be calculated from a table, which gives the quantity of water vapour contained in saturated air at different temperatures. Such a table may be found in any

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* This appears in Thomson's original paper, but is no doubt meant to imply that the gases leave the instrument 3° or 4° warmer than the liquid in the calorimeter.

book of chemical or physico-chemical tables, but, taking the latent heat of water vapour at 965° F. units, the total heat loss, either from evaporation of the water or from that carried off by the air itself, is so small that both together lie within the range of experimental error, half the total rise of temperature being taken for reference to the table.

"Lastly, the loss of heat through the apparatus should be taken into account, and as this will vary with the temperature of the surroundings, it is well to take the temperature of the water in the calorimeter immediately after the experiment, and having noted the duration of the experiment, to notice the loss of heat which takes place during a similar period, and add this on to the temperature of the water. It would, of course, be still more accurate to allow the temperature to fall to somewhere about the mean between the temperature at the beginning and at the end of the experiment, and then notice how much it loses during three or five minutes, which were taken to perform the experiment; but I have found the loss at the higher temperature not to exceed an average of about one-hundredth of a degree per minute."

The water equivalent of the apparatus used by Thomson was obtained by determining the weights of the different materials used and multiplying them by their respective specific heats. The following are the figures he obtained :—

TABLE XXXIV.—Calculation of Water Equivalent.

Material used.	Weight in grammes.	Specific Heat of Material.	Equivalent to Grammes of Water.
Weight of beaker = 7·812 ozs.,	221·472	·1977	43·784
Glass bell, . . .	48·015	·1977	9·492
Brass,	106·017	·09391	9·956
Iron, ...	12·993	·11379	1·478
Platinum, .	7·3496	·03244	·238
Clay support, ...	16·875	·1977	3·336
India-rubber, . . .	1·184	·2	·237
Mercury, . . .	27·192	·0333	·905
Thermometer glass,	4·161	·1977	·822
Copper gauze, .	27·122	·09515	2·581
Water employed, .	..	..	2000·000
Total material heated in the calorimeter equivalent to water, . . .	..	..	2072·829

It will be evident from these extracts of Thomson's original paper that he carefully examined all possible sources of loss of heat, and succeeded in producing what is undoubtedly a more scientific piece of apparatus than the Lewis Thompson, which was probably his object.

An alternative method has been used for determining the water equivalent of the apparatus, which obviates the many weighings as set out above.

The calorimeter is adjusted as used in a determination, and 2,000 grammes of water of a temperature different from the air are weighed out, and the temperature t noted. The temperature of the apparatus (*i.e.*, air temperature) $= t_1$. The 2,000 grammes of water are then poured into the glass cylinder, the other parts of the apparatus are placed in position, and the water kept well stirred for the length of time usually required for a combustion. The temperature is then taken $= t_0$. To correct for radiation losses the stirring is continued for an equal period of time, the final temperature being C. The loss due to cooling $=$ $(t_0 - C) = r$.

Then $$\frac{2{,}000\,[t - (t_0 + r)]}{(t_0 + r) - t_1} = \text{water equivalent.}$$

We do not like this method as described above. It would be better to have 1,000 c.c. of water in the vessel and then to add 1,000 c.c. at a different temperature. With glass vessels the method is not, in our opinion, good.

Brame and Cowan, in discussing the results obtained with this calorimeter, found that the *mean* results followed more closely those obtained by means of the bomb than the mean results of the other calorimeters used by them. The figures for a particular coal did not agree among themselves as well as had been anticipated, and these discrepancies ranged from 1·8 to 4·4 per cent. and from the bomb results by 1·8 to 6·9 per cent. Gray and Robertson found "the chief difficulty consists in regulating the current of oxygen so as to avoid loss of heat through imperfect cooling of the products, and at the same time to ensure that complete combustion is attained." They found the variations of the results of twelve different samples of coal were from 0·7 to 2·9 per cent. lower than those obtained by the bomb calorimeter, and suggest that the use of compressed pellets of coal may partially account for their more favourable results. The use of the compressed coal is recommended, as it ensures more uniform combustion, and of electrical ignition of the fuel. Another valuable recommendation by these authors is that the constants of the apparatus should be determined by "the combustion of a coal of average composition and known calorific value." * This is no doubt the best method of obtaining the water equivalent of the apparatus, as it enables such to be determined under the conditions similar to those for which the apparatus is employed.

Darling's calorimeter (Fig. 54), for using which the following instructions are issued, is, as will be readily seen, a modification of William Thomson's :—

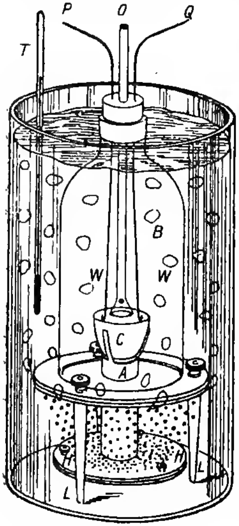

Fig. 54.—Darling's calorimeter.

"*Use of Calorimeter for Coal, Coke, Briquettes, and Solid Fuels generally.*—1. Carefully grind an average sample in an iron mortar, and weigh out 1 to 1·5 grammes in the crucible. Brush any particles from the sides into the mass at the bottom.

"2. Prepare a quantity of water at a temperature about 2·5° C. below the temperature of the room. Water drawn from a tap varies in temperature according to the season; but usually it will be necessary to add a little warm water to it in order to bring it to the requisite temperature. Measure out 1,400 c.c. into the vessel.

"3. Place the crucible in position, and fasten the glass cover down upon the rubber ring by means of the screws, so as to form an air-tight joint. The screws must only be turned until a resistance is felt; any further tightening might crack the glass cover.

"4. Insert the rubber cork into the neck so that the ignition-wire is embedded in the fuel. The copper wire should terminate about level with the rim of the crucible, and the tube delivering the oxygen about ½ inch above the surface of the fuel.

"5. Turn on a gentle stream of oxygen from a cylinder or gasholder, and immerse the apparatus in the water. Carefully

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* The difference between the results obtained from the 12 coals, and the bomb results were + 0·5 to − 1·8 per cent. when this method of determining the constants of the apparatus was employed.

note the temperature of the water,* and complete the battery circuit. As soon as the fuel is ignited, disconnect the battery. Allow the combustion to proceed steadily until completed, then continue passing the oxygen, mixing the water by lifting the combustion arrangement up and down, until no further rise of temperature is observed. Note the temperature carefully.

" *Precautions.*—(*a*) The oxygen must never be admitted so rapidly as to cause particles to be blown out of the crucible. The time required to burn 1 gramme of average coal in a steady stream of oxygen is about five minutes.

" (*b*) If the sample is observed to burn with a smoky flame, the combustion must be stopped, as the result will be valueless owing to unburnt carbon. A second combustion should then be performed with the end of the oxygen tube 1 inch below the cork until all volatile matter has burnt off, after which the tube may be pushed down to the crucible and the combustion completed.

" (*c*) During the combustion the tube delivering the oxygen should be moved about so as to ensure that every particle of coal is consumed. The flexibility of the rubber cork allows of this operation being easily performed. In every case near the end of the combustion, the supply of oxygen should be sufficient to cause the crucible to become visibly red-hot, whereby complete combustion is secured.

" 6. The calorific value is calculated as follows :—

$$\frac{(\text{Weight of water} + \dagger\text{water equivalent}) \times \text{rise of temperature}}{\text{Weight of fuel taken}} = \text{calorific value.}$$

" One cubic centimetre of water is taken as weighing 1 gram. If a Fahrenheit thermometer is used, the result will express British thermal units per pound of fuel ; if Centigrade readings are taken, the figure will represent either Calories per gram or pound—degree C. units per pound.

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* The thermometer sent out with the apparatus is graduated in $\frac{1}{20}$° C. or $\frac{1}{10}$° F., the range being from 5° C. to 40° C., or 40° F. to 105° F. Intermediate readings between the markings may be judged by the operator, or a more delicate thermometer may be used if desired.

† The figure expressing the " water equivalent " of the calorimeter and vessel is furnished with the apparatus. It is the weight of water which would absorb the same amount of heat as the apparatus.

"*Example.*—1 gram of Welsh steam coal burnt as above.
Water taken = 1,400 c.c. or grams.

$$\left.\begin{array}{l}\text{Water equivalent of}\\ \text{apparatus and vessel}\end{array}\right\} = 204 \text{ grams.}$$

Temperature of water before combustion = 14° C.
Temperature of water after combustion = 19·20° C.
Temperature of room = 16·6° C.
Calorific value =

$$\frac{(1,400 + 204) \times (19{\cdot}20 - 14)}{1} = 8,341 \text{ calories per gram,}$$

or 8,341 lbs. ° C. units per pound.
$8,341 \times \frac{9}{5} = 15,014$ British thermal units per pound.

$$\text{Evaporative power} = \frac{8,341}{537} = 15{\cdot}53.$$

"When an electric ignition is not available, place about ·05 gram of powdered sulphur on the weighed sample, and place the crucible and cover in position. Turn on a gentle stream of oxygen before inserting the cork and tube in the neck of the cover. The amount of oxygen passing may be judged by dipping the delivery tube under water. Now take the temperature of the water in the vessel, and ignite the sulphur by touching with a hot rod. Rapidly place the cork and tube in position, and quickly transfer the apparatus to the water. Proceed as before with the combustion.

"The correction necessary for the heat given out by the sulphur is 2,200 calories (gram ° C. units) per gram of sulphur; or 110 calories for ·05 gram. The correction, therefore, may be made by deducting 110 units from the final result in Centigrade units, or 198 when the Fahrenheit thermometer is employed.

"The error involved in this mode of ignition is slight, as practically no heat escapes from the apparatus during its transfer to the water. Any slight error on this score is nearly balanced by the temperature of the combustion apparatus being slightly higher than that of the water at the commencement of the experiment. In any case, the net error falls within the limit of accuracy of the experiment when a thermometer reading only to $\frac{1}{20}$° C. is employed. The sulphur ignition is very convenient, and gives results not differing sensibly from those obtained with an electric ignition."

The value of the water equivalent of this apparatus it will be noticed is issued with the apparatus, but we advise that, when once the facility of handling the apparatus is acquired, the equivalent should be determined by burning a fuel of a known calorific value. By doing this, one is enabled to determine the water equivalent under conditions similar to those which prevail when a determination is made.

Rosenhain's calorimeter (Fig. 55) is described as an improved form of Thomson's apparatus. It consists of a calorimeter vessel and a combustion chamber. The latter is formed of a glass lamp chimney closed at both ends by brass clamping plates, the joints being made by means of rubber washers. The plates are drawn together by means of screws on three wire uprights fixed to the lower plate.

The upper plate is fitted with a tube for conveying the oxygen into the combustion chamber, and also a stuffing-box, through which the wires for electrical ignition are carried.

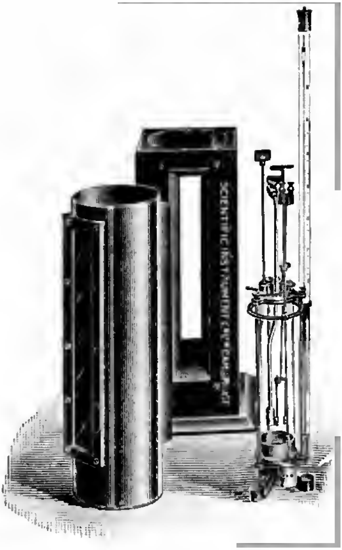

Fig. 55.—Rosenhain's calorimeter.

The interior of the combustion chamber is connected with the water of the calorimeter vessel by means of an aperture, which is closed by a ball valve; the products of combustion are thus allowed to escape, but the entry of water into the combustion chamber is prevented. If, however, it is desired that water be allowed to enter the combustion chamber, an arrangement is fitted whereby the ball may be raised. Two patterns of this instrument are made; in one the calorimeter vessel consists of a brass box with glass windows, the whole of which is enclosed in a wooden case to prevent radiation; in the other, the calorimeter vessel consists of a large glass beaker.

The advantages claimed for Rosenhain's calorimeter are :—

Accuracy.—Practically complete combustion is secured, less than ½ per cent. of the sample escaping combustion. When combustion is properly regulated no carbon monoxide is formed. When burning oils the standard pellets burn completely and rapidly, thus avoiding the risk of some of the oil remaining unburnt in the absorbent pellet.

Quickness.—A determination of the calorific value can be made in little more than half-an-hour. The combustion of 2 grammes of coal occupies about ten minutes.

Safety.—No parts of the apparatus are exposed to high pressure, and the risk of breakage is small.

Small Cost of Experiment.—A comparatively small quantity of oxygen is required, and the only breakable part is a glass chimney, which can be replaced by an incandescent gas-light chimney for a few pence.

Ease of Observation.—As the sample burns under observation its behaviour as regards caking and clinkering can be studied.

No Stirring required.—The water is agitated by the gas bubbling through it.

It is recommended that the water equivalent of the apparatus be ascertained by burning a known weight of coal of known calorific value, and this can be supplied if required.

This apparatus is simply constructed, and we are of opinion that it is an excellent modification of the Wm. Thomson apparatus, which, as we have already mentioned, does give good results when worked on lines similar to those here described.

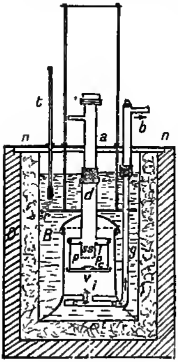

Fig. 56.—Fischer's calorimeter.

Fischer's calorimeter (Fig. 56) consists of a metal combustion chamber (of silver or nickel-plated copper), which is clipped to the bottom of a metal calorimeter vessel. The bottom of the combustion chamber is fitted with a flattened metal tube, which is carried up through the water of the calorimeter vessel; the extension of this tube above the water is made of glass. The calorimeter vessel is mounted in a wooden case, the annular space between the two vessels being packed with dry swansdown.

The joint between the calorimeter vessel and the wooden casing is coated with shellac varnish to prevent the absorption of moisture, and it is claimed that, if the apparatus be kept dry when not in use, the heat loss is very small, amounting to 0·0025° C. per degree difference of temperature per minute.

The apparatus is provided with a cover made in two halves, one of which is fastened by means of a screw, and carries the thermometer and the rods of the stirrer. The accompanying sketch shows the arrangement of the apparatus.

Oxygen is conducted into the inner chamber *p* by means of the glass tube *a*, which is connected with the metal tube *d*. The fuel which has been placed in the metal gauze basket *ss* burns, and the products of combustion pass through the gauze *c*, are forced round the metal plate *r*, and thus escape through *i* into the tube *c*, thence through *g*, and finally through *b* to waste, or, if desirable, *b* may be connected to a combustion apparatus, after the carbon dioxide, water, sulphur dioxide, etc., produced in the calorimeter have been removed by previously passing the issuing gases through soda lime, and calcium chloride or sulphuric acid tubes. The unburnt gases (if any) are converted into carbon dioxide and water, and the amount of unburnt fuel may be determined from the weights of these two compounds obtained. The ignition of the fuel may be made either electrically or by removing the cap from *a* and introducing a glowing splinter of charcoal.

Brame and Cowan, in their comparison of different types of calorimeters, found that the results obtained from this instrument, although agreeing well amongst themselves, the variation on the average amounting to only 1 per cent., were, when compared with the bomb, very disappointing. Of the five coals tested, in four cases this instrument gave the lowest results, and the average error compared with the results obtained by the bomb was found to be about 4 per cent. They also noticed a thin smoke when using this apparatus, and remark that Fischer states that when burning charcoal "the issuing gas contained both carbon monoxide and hydrogen."

These two authors noticed what no doubt all workers with this class of calorimeter have observed—namely, a blackening of the upper portion of the combustion chamber; and there can be no doubt that, generally speaking, the chief source of error in determinations of calorific power by means of calorimeters of this type is due to the difficulty of obtaining complete combustion of the volatile matter given off by the fuel. These are readily driven off at the commencement of the determination, and are not completely burned.

The following remarks, already published by one of us, fairly state our views on this and the former class of instruments :—

" It is true that with some kinds of bituminous coal fairly good results can be obtained with the various low-pressure oxygen calorimeters, of which William Thomson's is the earliest, and Rosenhain's probably the best, and certainly the most modestly described. It would be inadvisable, however, for a worker with any of these instruments to use his results for any other than internal purposes; it would be very rash to quote them against results obtained with a bomb calorimeter. The oxidising mixture type of calorimeter, such as Lewis Thompson's, is by no means useless, but usually unburnt solid carbon is left in the partly fused mass, and remains, with copper oxide, etc., when the alkaline salts are dissolved; an allowance should be made for this. The bomb calorimeter is, without doubt, the only one for serious work which is to bear challenge by other workers." *

III. High-Pressure Oxygen (Bomb) Calorimeters.—The bomb calorimeter is undoubtedly the most satisfactory apparatus for determining the calorific value of fuel, and its best forms possess the following advantages over the different calorimeters previously described :—

(i.) The materials employed in its construction are almost entirely metallic, the exception being the enamel lining of the bomb which is present in some patterns. The metal used for the bomb proper is either steel or delta metal with comparatively small amounts of platinum; and that for the calorimeter vessels and stirrers is usually either copper or brass.

The specific heats and conductivities of these metals are well known, and it is obvious that these offer great advantages compared with glass, which is largely used in practically all of the other forms of calorimeter.

(ii.) The combustion of the substance is complete, provided that due precautions are observed that the substances to be burned are introduced into the bomb in a suitable condition. This point will be dealt with in describing the combustion method of determining the water equivalent.

(iii.) The thermal effect of the surroundings is reduced to a minimum by means of an annular water jacket which surrounds

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* *Chemical World*, vol. i., pp. 3, 75, 1912.

the calorimeter, and, moreover, the sign and magnitude of this effect may be readily determined.

(iv.) The heat effect due to the formation of sulphuric and nitric acids is easily ascertained by determining the amount of the acids in the washings of the bomb after a determination of calorific power.

(v.) The bomb is available for all fuels—solid, liquid, or gaseous.

With regard to this last point, it may be pointed out that M. Berthelot, who originally designed this form of calorimeter, used it only for gases at first, but, with the assistance of M. Vieille, subsequently modified it for use with solids and liquids.

The only disadvantage associated with it compared with other forms of calorimeter is that of cost, but this during recent years has been greatly reduced. Probably as the demand for accurate calorimetric work increases, the cost of such instruments will become less.

Berthelot's bomb (Fig. 57), as we have already stated, was the first of this class of calorimeter, and although it has been modified by numerous workers, the principle underlying the method is unchanged; with one exception (Mahler-Kröcker) the modifications introduced are, one might say, trivial so far as design is concerned. On the other hand, they are important when the question of cost is considered. The "bomb" proper—that is, the combustion chamber—consists of a steel chamber constructed to withstand a pressure of 250 to 300 atmospheres, to which is fitted a steel cover. In the accompanying figure (Fig. 57) we give a sectional drawing of the bomb cover. *R* is a screw head which regulates the flow of oxygen gas into the bomb by means of the conical valve; the lower end of the delivery tube is turned up so as to prevent the combustible substance *m* from being blown out of position by the entering gas.

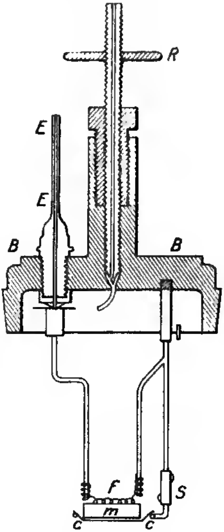

Fig. 57.
Berthelot's bomb cover for solid fuel.

E is an insulated platinum rod which passes through the bomb cover, and from which a fine platinum wire *f* passes to another platinum rod attached to a support *S*, which carries a small tray or crucible in which the combustible matter *m* is placed. *S* is in metallic connection with the bomb cover *B*, and by touching any part of the cover with one wire from an electrical battery and *E* with the other terminal the wire *f* is heated to incandescence, and this fires the combustible which, in the presence of a large excess of compressed oxygen, is burned completely and almost instantaneously.

The interior of the bomb and cover is *lined* with platinum, and Berthelot remarks in his book previously referred to, "It is not sufficient to have the steel surface platinised by electro-deposition, as this does not sufficiently protect the steel from being attacked by the products of combustion." The porosity of gold plating is also referred to as being unsatisfactory for this purpose.

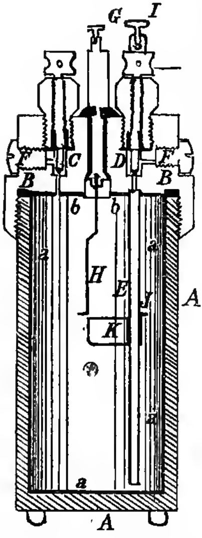

Fig. 58.—Mahler-Kröcker calorimetric bomb (section).

The bomb cover fits gas-tight on to the bomb; the platinum surfaces being comparatively soft, assist in making a sound joint, and a steel cover provided with a thread which engages a similar thread on the outside of the combustion chamber is screwed well down to ensure an absolutely gas-tight joint (*cf*. Fig. 33).

Mahler modified the Berthelot bomb by substituting for the costly platinum lining one of enamel capable of resisting the action of the products of combustion. This renders the apparatus less costly, but the durability is obviously diminished, and once the enamel has cracked it is no longer possible to protect the steel of the bomb from the action of the acids produced during the combustion.

The Mahler-Kröcker is one of the best forms of bomb calorimeter. The bomb (Fig. 58) is cylindrical, and its cover is more elaborately constructed than that of Berthelot. In this form two valves communicate with the combustion chamber, one of which opens direct to the top, and the other, by means of a platinum tube, to the bottom of the bomb. The object of this arrangement is to enable one at the finish of the ordinary calorimetric determination to allow the products of combustion to pass through a system of weighed absorption tubes, so that the amount of water produced during the combustion may be ascertained; the *net calorific* value of the fuel is calculated from this determination.

This appears to be the *raison d'être* of the constructional modification of this pattern bomb, but it does *not* enable one to determine accurately the amount of water produced owing to the fact that the sulphuric acid formed during the combustion combines with some of the aforesaid water, and it is consequently impossible to determine the latter under the conditions stated.

This bomb is, however, a very convenient form of apparatus, and the facility of handling it is much more pronounced than in some other patterns, which are constructed on much heavier lines, and are consequently more difficult to manipulate.

The bomb *A* consists of a nickel-plated steel shell, on the upper external surface of which a bold screw thread is cut. It is fitted with a cover or cap *B*, on the inner surface of which a female thread, of the same pitch as *A*, is cut. The bomb is lined with enamel *a*, and the cover in the best form of this apparatus has a sheet-platinum lining *b*. The cone-valves *C*, *D* are iridium-pointed, and are opened or closed by screw spindles, the gas entering or leaving the bomb by tubes closed by screw plugs *F*. The valve *C* opens directly into the top of the bomb, whereas *D* is connected with a platinum tube *E* reaching nearly to the bottom. This tube supports a platinum crucible *K*, in which the fuel is placed, and is also connected with one of the terminals *I*, the other terminal *G* is insulated and is continued inside the bomb by the platinum wire *H*. In some patterns of this apparatus the platinum crucible is replaced by one of clay, which is suspended from two projecting spurs on *H* and *E*. The bomb is kept well off the bottom of the calorimeter by three steel pegs 12 mm. high.

Firing is effected by means of a fine platinum or nichrome wire about 0·1 mm. diameter, which is fixed to *H* and *E* respectively, and which is looped so as to be in contact with the fuel in the crucible.

Our practice is to stretch the wire taut between the two platinum conductors, and to tie a piece of cotton of known weight on the wire, the free end of the cotton being buried in the fuel.

Iron wire is sometimes used for firing purposes, but it is not considered as satisfactory as platinum, owing to the injury caused to the lining of the bomb by particles of fused ferric oxide.

The platinum wire, although more expensive than the iron, is detached after a determination, and may be readily converted into platinic chloride for use in the laboratory. The edge of the bomb is slightly grooved, and a lead washer in the cover fits into the groove, thus making a satisfactory gas-tight joint.

The platinum tube *E* is *very* thin. We have found that a silver collar about 25 mm. long, made by drilling a piece of ordinary sterling silver rod, 6½ mm. diameter, sweated round the upper part of the tube, gives great protection. This has since been strengthened at the lower end by a conical "blob" of soft solder round the platinum tube. The high conductivity of the silver prevents the melting of the solder by local heating.

The bomb, which is 220 mm. high over all, is stood in a nickel-plated copper (or brass) cylindrical calorimeter vessel, 250 mm. high and 140 mm. diameter, with two small wire handles towards the top. This will conveniently hold 2½ litres of water when the bomb is *in situ*. A triple horse-shoe stirrer is worked by a crank gear (see Fig. 62). The calorimeter vessel is placed on a slip of ebonite, which insulates it so far as heat is concerned from the bottom of the large annular copper vessel in which it stands, and which holds about 30 litres of water. The top of this vessel carries the supports for the stirring gear and a clip to hold the thermometer. The inner surfaces of the vessel are "enamelled" white, and an ebonite cover protects the surface of the water in the calorimeter from adventitious draughts or other causes of irregularity.

A large spanner, which fits over the rectangular block, carrying the valves, etc., on the top of the bomb cover, is used for tightening and loosening this cover, which must be screwed and unscrewed with great care. This very large but rather fine screw thread needs gentle handling, and should be kept lightly greased, besides being cleaned after use with a wire scratch brush.

The "Sarco" bomb calorimeter consists of a very heavy bomb made of delta metal,* the cover being bolted down by means of three nuts working on screw studs deeply sunk into the metal of the bomb. The gas is admitted into the bomb by an arrangement similar to that of Berthelot, and the means for igniting the fuel are also similar. The interior surfaces are heavily gilt, and finally platinised, in order to increase the durability of

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* Approximately, Cu 56, Zn 42, Fe, Pb, etc., 2.

the lining. In this pattern the lead washer is sunk in the bomb, a projecting finished rim of the bomb cover fitting down on it. The bomb fits on to a brass cage, which serves to keep it from touching the bottom of the calorimeter vessel; the revolving stirrer supplied can hardly be described as of the helical pattern, but we have found that it is quite efficient, although no more so than the horse-shoe pattern, and the latter is more advantageous in the respect that it is easier to fire the charge when all is ready without stopping the stirring, and that the thermometer can be more conveniently placed in the instrument. The annular water jacket which surrounds the calorimeter has a capacity of about 8 litres of water, whereas that supplied with

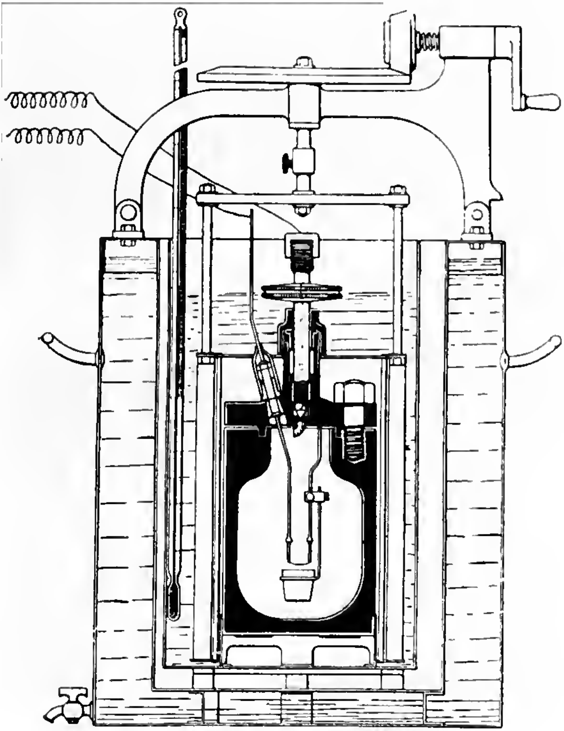

Fig. 59.—" Sarco " bomb calorimeter.

the Mahler-Kröcker is better in so far that the water capacity is about three times greater. With regard to the question of the *enceinte* of these different calorimeters, it should be stated that it is much better always to have an annular water jacket, although wooden insulating cases are sometimes supplied, the cost of the apparatus being thereby reduced. This point has been dealt with in Chapter VI.

Our experience of both the Mahler-Kröcker and the Sarco bomb is that they are excellent instruments, and the results obtained are such as to give one the greatest confidence. The latter, however, is not so easy to manipulate when determining the sulphuric and nitric acids produced, the bomb being very heavy and more awkwardly shaped. In the case of the Mahler-Kröcker the rinsing out of the bomb is as easy to manage as if using a beaker.

The Mahler-Kröcker bomb is more convenient for use with gases, as the valves can be closed without turning either the bomb or the gas connection. It is also easy to pass air through it, if it is desired to collect the products of combustion. It appears, at first sight, that it is also an advantage to be able to fill the bomb by passing through it the gas to be burnt, but we think few people who had troubled to purify a gas would care to be so wasteful.

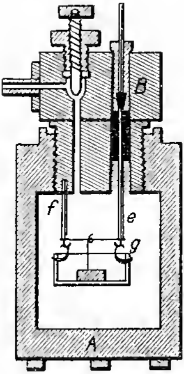

Fig. 60.—Hempel's bomb calorimeter.

The Hempel bomb (Fig. 60) consists of a cast-iron chamber *A* with an enamel lining, and a large head piece *B*, which is screwed into the neck of the combustion chamber. The joint between the head and the combustion chamber is rendered tight by means of vulcanite or lead washers.

Two stout pieces of iron rod *f*, *e* are fixed to the head, one being fastened into the metal, the other being continued right through the head and insulated from the surrounding metal, so that it may be used for the electrical ignition of the fuel.

A screw valve is also fitted for regulating the admission of oxygen.

The lower ends of the two rods are fitted with two stout pieces of platinum wire bent upward in the form of hooks, from which is suspended the capsule or basket containing the weighed quantity of fuel. The ignition of the fuel is made by stretching a *fine* platinum wire between the two stout platinum ends, tying a piece of thread to the middle of the wire, and arranging the other end so that it is in intimate contact with the fuel. The metal calorimeter vessel is hung in a wooden vessel, a space of about 2 cm. being allowed between the calorimeter vessel and the wooden jacket. This is an inexpensive piece of apparatus, and good results may be obtained with it. Mr. G. N. Huntly found that by standing the bomb on a wire cage in the calorimeter vessel he obtained better results; the short pegs fitted to the particular Hempel bomb he used did not allow of sufficiently good mixing of the water, and the results were not so concordant as those obtained when the bomb was raised by means of the device mentioned.

Method of Using Bomb Calorimeters.—For the determination of the calorific value of a fuel by means of a bomb calorimeter about 1 gramme of the very finely powdered air-dried coal is weighed out in a small 000 porcelain crucible, which is placed in the platinum crucible of the bomb.

A fine platinum or nichrome wire is stretched between the firing terminals inside the bomb, and cautiously tested with the battery to make sure that the connections are sound.

A short length of cotton thread is tied at the middle of the wire, the loose end being imbedded in the fuel.

Ten grammes of distilled water are placed in the bomb, and the edge which comes into contact with the lead washer may be carefully smeared with a trace of heavy mineral oil, so that none of it appears inside the bomb. The object of this is to prevent the hard finished edge from "*jambing*" into the lead; in the case of the Mahler-Kröcker the omission of this precaution has rendered the subsequent unscrewing of the bomb after a determination a most laborious operation.

The bomb cover is now placed in position and screwed down until it is felt to be well home.

The oxygen admission valve is now connected to the gas supply and oxygen admitted at a gentle rate until the pressure gauge registers 25 atmospheres. The valves are then screwed down *without any undue force being applied*—hand pressure alone should suffice to close the small valves—and the gas supply shut off. The bomb is now placed in the calorimeter vessel, which contains, say, 2,490 grammes of water—making 2,500 grammes with that inside the bomb—and allowed to stand for, say, five minutes. No bubbles of gas should escape from the bomb when immersed ; after the lapse of a few minutes the thermometer is placed in position and the stirrer started. Readings of the thermometer at minute intervals are taken, and when the temperature is stationary, or is seen to be rising or falling at a uniform rate, the electrical connection is completed to the bomb terminals. In about 10 to 15 seconds the temperature is seen to rise, and this continues rapidly for about two minutes, after which it rises very slowly for about another two minutes, and then commences to fall. The fall soon becomes uniform, and about five subsequent readings at minute intervals should suffice for the cooling correction. The two following examples may be taken as typical of the course of a determination :—

TABLE XXXV.

No. 1. Determination with Benzoic Acid (Surco bomb).			*No. 2. Determination with Benzoic Acid (Mahler-Kröcker).*	
Min.			Min.	
0,	13·870° C.	*Preliminary Period.*	0,	19·200° C.
1,	13·870° C.		1,	19·200° C.
2,	13·870° C.		2,	19·200° C.
3,	13·870° C.		3,	19·200° C.
4,	14·700° C.	*Principal Period or Combustion.*	4,	20·450° C.
5,	15·700° C.		5,	21·370° C.
6,	15·780° C.		6,	21·440° C.
7,	15·785° C.		7,	21·442° C.
8,	15·780° C.		8,	21·434° C.
9,	15·775° C.	*Final or Cooling Period.*	9,	21·425° C.
10,	15·765° C.		10,	21·415° C.
11,	15·760° C.		11,	21·405° C.
12,	15·750° C		12,	21·396° C.
			13,	21·487° C.

Correction for Formation of Sulphuric and Nitric Acids in Bomb.—When the determination is finished, the bomb is removed from the calorimeter, the valve is opened, and the gas allowed to escape, the bomb cover is removed and both bomb and cover are washed out with distilled water, the liquid being collected in a beaker for the determination of the *sulphuric* * and nitric acids

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* If this acid is likely to be present, which is, of course, not so with benzoic acid.

produced. A careful inspection of the washings will at once show if the combustion has been satisfactory. There should be no evidence of unburnt carbon. The liquid in the beaker is titrated with a standard solution of decinormal alkali, using methyl-orange as an indicator, the number of cubic centimetres of alkali required being noted.

The liquid is made distinctly acid with hydrochloric acid, filtered, and the filtrate heated to boiling. Barium chloride solution is added, and when the precipitate shows signs of settling the whole is allowed to stand. When the supernatant liquid is clear the precipitate of barium sulphate is filtered off, washed with hot water, ignited, and weighed. The barium sulphate obtained multiplied by 0·1374, the logarithm of which is $\bar{1}\cdot1379$, gives the weight of sulphur in the weight of fuel taken.

We have now the means of correcting the observed value for calorific power for the heat evolved owing only to the circumstances under which the combustion is conducted in the bomb. Not only has all the carbon been burnt to carbon dioxide and the hydrogen to water, but the sulphur has been burnt, not merely to sulphur dioxide, which is the normal product of the ordinary combustion of sulphur in air, but to the trioxide, which has further combined with water to form sulphuric acid. This acid has also given out some heat in dissolving in the water at the bottom of the bomb. Further, the high temperature of combustion has led to the formation of some nitric acid by the direct union of oxygen and (probably) atmospheric nitrogen from the air left in the bomb, and the subsequent solution of the N_2O_5 produced. The combustion of 1 gramme molecule of sulphur to SO_2 is accompanied by the evolution of 72 Calories. The combustion of the same amount of sulphur to SO_3 and the solution of the product in a large excess of water gives rise to an evolution of 143 Calories. Hence the excess heat obtained in the bomb experiment due to this cause is $(143 - 72) = 71$ Calories per gramme-molecule.

Now, 1 gramme-molecule of sulphur in burning produces as much sulphuric acid as will neutralise 2 litres of normal alkali, so that 1 c.c. of $\frac{N}{10}$ alkali neutralised by *sulphuric acid* in the washings from the bomb will represent—

$$\frac{1}{20{,}000} \times 72 \text{ Calories, or } 3\cdot6 \text{ (small) calories } (\log = 0\cdot5563).$$

One gramme-molecule of nitric acid in aqueous solution is formed from nitrogen, oxygen, and water with evolution of $\frac{28\cdot6}{2} = 14\cdot3$ Calories. 1 c.c. of $\frac{N}{10}$ alkali neutralised by the nitric acid in the bomb washings, therefore, corresponds to an excess heat of

$$\frac{14\cdot3}{10{,}000} = 1\cdot43 \text{ (small) calories (log } 0\cdot15534\text{).}$$

Now, if we multiply the weight of barium sulphate obtained by 0·1374 (log $= \bar{1}\cdot13792$), we get the weight of sulphur in the amount of fuel taken; from this the percentage of sulphur, which it may be desired to return, can be calculated. If again we multiply the weight of barium sulphate (in grammes) by 85·48 (log 1·93186), we get the number of c.c. of $\frac{N}{10}$ alkali neutralised by the sulphuric acid formed. The remainder of the alkali used in the experiment was, therefore, due to nitric acid.

In an actual example 1 gramme of fuel was burnt and the washings of the bomb neutralised 9·0 c.c. of $\frac{N}{10}$ alkali. The weight of $BaSO_4$ was 0·0503 gramme.

$$\begin{array}{rrl}
\text{Log } 0\cdot0503 = & \bar{2}\cdot6993 & \\
& \bar{1}\cdot1379 & \\
\hline
& \bar{3}\cdot8372 & = 0\cdot00687 \text{ gramme sulphur} \\
& & = 0\cdot69 \text{ per cent.} \\
& \bar{2}\cdot6993 & \\
& 1\cdot9319 & \\
\hline
& \cdot6312 & = \ 4\cdot28 \text{ c.c. } \tfrac{N}{10} \text{ for sulphuric acid.} \\
& \cdot5563 & \\
\hline
& 1\cdot1875 & = 15\cdot6 \text{ calories for sulphuric acid.}
\end{array}$$

9·0 — 4·28 = 4·72 c.c. for nitric acid.

$$\begin{array}{rrl}
& \cdot15534 & \\
\log 4\cdot72 = & \cdot67394 & = 6\cdot79 \text{ calories for nitric acid.} \\
\hline
& \cdot82928 &
\end{array}$$

Total correction for excess heat = 15·6 + 6·8, or 22·4 calories. This is to be deducted from the total evolution of heat measured in the bomb after all other corrections have been applied.

It is, we think, as well to state that, although the whole calculation can be done on an ordinary 10-inch slide rule in a few minutes, the upper rule even will give sufficient accuracy for the purpose.

Ordinary combustion of sulphur itself leads only to the formation of sulphur dioxide, and it is certain that at least the heat evolved in this process should be credited to the fuel; it is not at all certain that when a mixed fuel containing only a small proportion of sulphur is burnt, the product is not really SO_3. The burning of ordinary coal gas or mixed coal and carburetted water gas containing sulphur, leads to the formation, not of the dioxide, but of the trioxide, unless the products are artificially cooled immediately after leaving the flame. One never smells SO_2 near an ordinary flat-flame burner, but it is usually very distinctly perceptible in the exit gases from a gas calorimeter. If all the sulphur were burnt to SO_3 in the combustion of a fuel, then the deduction from the heat of formation of dilute sulphuric acid from sulphur, oxygen, and water, 143 Calories per gramme-molecule (*vide supra*), would need to be reduced only by the heat of solution of SO_3 in an excess of water—*i.e.*, by about 40 calories; and 1 c.c. of $\frac{N}{10}$ alkali neutralised by the sulphuric acid would indicate that an excess of 2·0 (small) calories had been measured in the calorimetric experiment. The former view that SO_2 only is formed by the combustion in a furnace of sulphuric fuel is that usually accepted, but we feel that the possibility of a slightly different state of affairs should be indicated.

The correction due to cooling has been previously fully described (p. 188), and there only remains the correction to be made for the heat of combustion of the cotton thread used for firing. If a thread weighing 2 milligrammes is used the correction to be made is 8 calories, the heat of combustion of cellulose being 4,208 calories per gramme. The amount of heat due to the heating of the fine platinum wire is insignificant, and may be neglected.

The accompanying figures (61 and 62) from photographs show the general arrangement of the apparatus used by us.

The following detailed description may be of use:—

Arrangements for filling Bombs with Oxygen from Cylinders.—In Fig. 61 a bomb is being filled from a single cylinder, with which it is connected by small thick-walled copper tubing. A pressure gauge joined to a branch of this tubing indicates the pressure of gas in the bomb. Behind this another bomb is connected up to two cylinders. Thus a partly emptied cylinder can be used for passing oxygen into the bomb until no more gas will flow. This cylinder is then shut off and the other less empty cylinder is used for filling until the requisite pressure of 25 atmospheres is indicated. The various appliances used for tightening up the joints between the bomb and its cover and for weighing the water in the calorimeter vessel are shown.

Care should be taken that the nut connecting the supply pipe to the bomb is turned with the screw head or some of the oxygen may escape from the bomb.

The wooden stand to the left of the bomb is shaped to receive the bomb when tightening and unloosening the cover.

The two cylinders at the back of the table are each connected, by a flexible stout-walled copper tube to a metal mixing chamber, which is connected with a pressure gauge; the delivery tube from the latter is fitted with a screw plug for insertion into the bomb as shown. When the requisite pressure is obtained, the entry of oxygen into the bomb is closed by screwing down the valve shown nearest the delivery tube. The object of the two cylinders coupled up, as shown, is to prevent waste of oxygen. Once the pressure in a *single* cylinder has fallen below 25 atmospheres it can no longer be used for filling the bomb, but if used in connection with another freshly filled cylinder, one can get as much as possible out of it, and complete the filling of the bomb up to 25 atmospheres from the new one, care, of course, being taken to shut off the partially filled cylinder before opening the new. This method of procedure can be followed until one cylinder is emptied, when it is disconnected and replaced by a fully charged one.

The balance shown weighs up to about 5 kilos., and is sensitive to 0·05 gramme; this is a convenient size, as it is large enough to take the calorimeter vessel easily and strong enough to weigh the vessel with its contents of 2500 grammes of water.

Bomb Calorimeters with Stirring Gear driven by Electric Motor.—On the left is a calorimeter with helical rotating stirrer, shown at the side; the gold-lined delta metal bomb, with the cover removed and placed in front of it, is shown to the right of the calorimeter vessel; a spare bomb with its cover bolted on is shown on the shelf in front of the minute clock. The small porcelain capsule in which coal is burnt, and the support for the bomb when in the calorimeter, are shown in the foreground. On the right is shown a calorimeter with up-and-down horse-shoe stirrer (taken out and placed at right of calorimeter). The steel, porcelain-lined

PLATE VIII. [To face p. 256.

Fig. 61.—Apparatus for filling Bomb with Oxygen.

Fig. 62.—Bomb Calorimeter, with Stirring Gear driven by Electric Motor.

beaker-shaped bomb and its cover, with a platinum crucible and silica cup for use in the bomb, are also shown. The water vessel of this calorimeter is shown behind the delta metal bomb in the centre of the picture. A telescope for reading the thermometer is also shown.

There are many other modifications of the bomb calorimeter, which, as we have already stated, do not differ in principle from that originally designed by Berthelot.

Féry's thermo-electric bomb (Fig. 63) is described in the *Comptes Rendus*, vol. cliv., pp. 691-693, 1912.

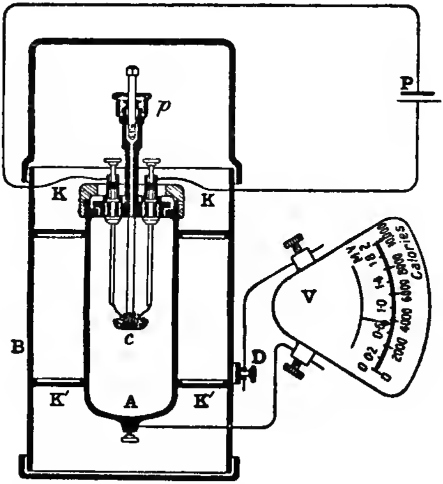

Fig. 63.—Féry's thermo-electric bomb calorimeter.

The following description of this instrument is condensed from a paper read at the meeting of the British Association at Dundee, September, 1912, by Robert S. Whipple, M.I.E.E.

"The instrument is not dissimilar to the well-known Mahler calorimeter, with the exception that the bomb is much lighter and there is no water jacket. Fig. 63 shows the construction of the instrument. The bomb *A*, in which combustion takes place, is a cast-iron vessel weighing about 1 kilo. and having a capacity of about 250 c.c. It is supported by two constantan discs, *K* and *K′*, of about 1 mm. in thickness, the discs being soldered both to the bomb and to the brass surrounding-vessel *B*. The cover of the bomb is held in position by means of the collar (shown in section), which fits over the top of the bomb in a somewhat similar manner to that in which a breech fits a modern gun. The coal to be tested is placed on the small tray *C*, and is ignited by means of a piece of cotton resting on the nickel-chromium heating wire connecting the two terminals in the cover, the latter being connected to the battery *P*. Oxygen at 200 lbs. pressure is introduced into the bomb through the needle-valve *p*.

"The constantan discs and the bomb act as a thermo-couple, the iron of the bomb forming the hot junction, the brass surrounding vessel the cold one. The E.M.F. thus generated is measured by the voltmeter *V*.

"The weight of the bomb is only 1 kilo., and there is no water, so that its water equivalent is very small. As a result, the temperature rise due to the combustion of 0·5 gramme of coal is about 20° C. The pointer galvanometer employed gives approximately a deflection of 60 mm. for 800 microvolts (20° C.), so that it is possible to estimate the temperature rise to within 0·2° C., or to $\frac{1}{300}$ of the total rise in temperature of the bomb. The simplicity of the method of reading the temperature as compared with the difficulty of reading finely divided mercury thermometers will be appreciated by all those who have worked with the latter.

"The loss of heat from the bomb is due to three causes:—

"1. Conduction along the constantan discs.

"2. Convection by the air currents in the space surrounding the bomb; and

"3. Radiation from the walls of the bomb to the surrounding shell.

"Considering the first cause—conduction would simply tend to lower the temperature to which the bomb would rise if the supporting discs were non-conductors. The rate of loss of heat by conduction may be assumed to be proportional to the difference in temperature between the centre and circumference of the discs.

"Convection currents are not easily established in a closed space. When established the heat losses due to this cause are approximately proportional to the square of the difference in temperature between the bomb and the surrounding air.

"The losses due to radiation at the comparatively low temperature to which the bomb is heated are very small. In the small range of temperature (not more than 30° C.) Newton's law of cooling must be an excellent first approximation: this means that the rate at which heat passes by radiation from the walls of the bomb to the surrounding vessel is practically proportional to the difference between the temperatures of these two bodies.

"Curves obtained from a series of readings taken with the calorimeter show, firstly, that the portions showing cooling are of the exponential type, and, secondly, that it is possible to deduce in a simple manner the temperature to which the calorimeter would have risen had there been no heat losses.

"This ideal temperature, so to speak, can be calculated by allowing for the loss of heat in each quarter minute of combustion, but as this loss is roughly proportional to the maximum temperature attained, the curves are practically of the same shape, allowing for differences of scale, so that this ideal temperature is a constant multiple of the highest temperature reached.

"It was found that with the exception of an experiment in which a relatively low pressure (100 lbs.) was employed, the coal was completely burnt; in this latter experiment the combustion was also not so rapid, and hence the same high temperatures obtained with the other pressures were never reached. Experiments show that the values obtained agree amongst themselves to within 3 per cent. so long as the gas pressure was between 150 lbs. and 250 lbs. per square inch.

"Experiments were made to determine the effect of variations in the weight of coal burnt. The maximum temperature was found to take place within two minutes from the time of ignition in the case of all samples with the exception of the largest one (0·8 gramme), some ash left in the pan showing that in this case there was insufficient oxygen to give complete combustion.

"Experiments have been made with materials of largely differing calorific values, and the results have been found to agree excellently amongst themselves. Sugar carbon (calorific value 8,070), paraffin oil (14,000), and benzoic acid (6,330) have all shown that the deflections of the galvanometer are proportional to the calories dissipated in the bomb. In the case of the instrument tested the dissipation of 100 calories gives rise to an E.M.F. of 105 microvolts, and this value per 100 calories is found to be practically constant up to 10,000 calories.

"As now constructed the bomb is made of cast iron unprotected by any lining such as enamel or platinum. There should be no difficulty in fitting such a protective device, the only drawback being that such arrangements are apt to introduce temperature lag.

"The scale of the galvanometer is divided in millivolts and also in calories on the assumption that a sample weighing 0·5 gramme has been burnt. There is thus no necessity to determine the water equivalent of the calorimeter nor to read the rise in temperature (as is usually done); the calorific value of the coal is found by a single observation. A slide rule will readily convert the values obtained if a slightly different weight of coal has been used. It will be found that if the sample of coal has been weighed previously a complete experiment can be made in less than five minutes.

"The instrument is easy to handle, there are no fragile parts, and it is essentially a practical tool."

Gross and Net Values for Solid Fuel.—The calorific power of a fuel is returned either as a "gross" or a "net" value; in the former case it represents the whole of the heat produced by the combustion of the fuel, all the products of combustion being cooled to the temperature prevailing in the calorimeter vessel at the end of the determination.

In the case where the "net" value is returned a deduction is made from the "gross" value, the magnitude of the deduction depending upon (*a*) the amount of moisture present in the air-dried sample, and (*b*) the amount of water produced by the combustion of the hydrogen of the so-called "coal substance." The latter figure is obtained from the ultimate analysis of the fuel, the percentage of hydrogen multiplied by nine gives the approximate amount of water produced. The most recent determinations of the atomic weights reduce this multiplier to 8·94.

Having these details, we are in a position to make the necessary correction for loss of heat due to the *escape of the water as steam.*

In a previous chapter we have shown that the amount of heat necessary to convert *water* at 100° C. to *steam* at 100° C. is about 540 calories per gramme, this figure being known as the latent heat of steam; in addition to supplying this amount of heat, we have also to raise the water from the temperature of the air—whatever it may be—to 100° C. This is usually assumed to be 80 calories per gramme, the average air temperature being reckoned as about 20° C.* Therefore, for every gramme of water in the coal, whether present as such or produced during combustion (540 + 80) = 620 calories are deducted.

Thus the *net* figure, as returned, represents the available heat, after allowing for loss due to the vapourisation of the water *as steam at* 100° *C.* This figure, however, does *not* represent the total loss of heat due to this amount of water, because, in actual practice, the steam leaves the boiler flues at a much higher temperature than 100° C., the actual temperature depending upon the construction of the furnace, etc., and also upon the efficiency of the stoking.

We may assume that the temperature of the flue gases is about 600° F.—*i.e.*, about 315° C.

Taking this estimate as correct, we can arrive at a very rough estimate of the total heat of the dry steam by assuming that its mean specific heat, S_{100}^{315}, between 100° and 315° is

$$\frac{S_{100} + S_{315}}{2}.$$

Holborn and Henning (*P.T.R.*, 1907) give the following formula for the specific heat of water vapour between 100° and 1,400° at constant pressure :—

$$S\,c\,p = \cdot 4669 - \cdot 0000168\,t + \cdot 0_7 44 t^2.$$

The specific heat at 100° is ·4652
„ „ 315° is ·4660

The mean specific heat is ·4656

$$\cdot 4656 \times 315 - 100 = 100 \cdot 1.$$

That is, the total heat carried away is about 100 calories more than is assumed in the usual calculation.

In addition to this, no notice is taken of *other inevitable losses* which occur when burning fuel in actual practice, such as the heat lost by raising the temperature of the air necessary for the combustion of the fuel to that of the flue gases. This may amount

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* The latent heat of steam is probably not below 538 calories at 100° (*cf.* p. 130). The total heat (*i.e.*, cooling to 0°) at this temperature is probably about 639 calories.

to nearly 20 per cent. of the "gross" calorific value of the coal. Then we have losses of heat due to unburnt coal in the ashes, radiation, and the possibility of incomplete combustion resulting in the production of some carbon monoxide.

It will be seen, therefore, that the inevitable loss of heat due to the vapourisation of the water is only one of several such losses, and it appears to us to be a far more rational proceeding to return the *gross* calorific power of a fuel, and to supplement this figure with as much information as may be required. This would vary for different purposes; clearly the analyst when called upon to examine the coal could do no more than give its proximate and ultimate composition, since all the other figures depend on the way it is burnt in the furnace, if a "heat balance" were to be made it would be necessary to know, in addition to the ultimate analysis of the fuel, the composition of the flue gases, the amount of ashes obtained, and the percentage of carbon contained therein, the temperature of the air and of the flue gases, and the relative humidity of the air. The expression "net" value is not what it is pretended to be, and it is difficult to see what advantages ensue from such a method of returning calorific values.

If desirous of using this method of returning calorific power, the two following formulæ for obtaining the amount of water produced by the combustion of the hydrogen present may be found of value, as it is claimed that the ultimate analysis of the fuel is rendered unnecessary.

Mr. C. A. Seyler proposes a formula—

$$H = 1{\cdot}72 + 2{\cdot}43 \log V,$$

where V = volatile matter in the *water and ash-free coal.*

"This means that the hydrogen is proportional to the log of the volatile matter, or that, as the hydrogen increases in arithmetical proportion, the volatile matter increases in geometrical ratio. From the volatile matter we may, therefore, infer the percentage of hydrogen approximately or (*vice versâ*), but not the carbon."

The following is an abstract from *Journ. Soc. Chem. Ind.*, July 15, 1912:—

*Net Calorific Power of Fuels (Coal and Coke) calculated from the Results obtained by the Bomb Calorimeter and the Proximate Analysis.**—"From the results of the ultimate and proximate

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* R. Lucion, *Bull. Soc. Chem. Belg.*, vol. xxvi., pp. 255-262, 1912.

analyses of 63 samples of coal (including lignites, bituminous coals, and anthracites) from various countries, the percentages of volatile matter (as determined at 100° C.) and hydrogen in the respective 'coal substances'—*i.e.*, the materials free from moisture and ash—were calculated. The percentages of water of combustion (obtained by multiplying the figures for hydrogen by 9) were then compared with the corresponding percentages of volatile matter, a series of coefficients (N) being obtained by dividing the former by the latter.

"The samples being grouped according to their character and origin, average values for each group were obtained, from a selection of which a curve was plotted, the ordinates (N) being 0·91, 0·99, 1·16, 1·24, 1·24, 1·35, 1·47, 2·04, 2·34, 2·66, and 3·71, and the corresponding abscissæ (percentage of volatile matter) 59·2, 49·5, 41·1, 38·5, 37·5, 35·0, 31·0, 19·75, 16·6, 13·8, and 6·65 respectively.

"For calculating the net calorific power (P′) of a coal the formula $P' = P - 6\ (M + N\ V)$ is employed, P being the gross calorific value as determined by the bomb, M and V being percentages of moisture and volatile matter, respectively, in the sample, and N the coefficient (ascertained by reference to the curve) corresponding to the percentage of volatile matter in the coal substance of the sample. The net calorific power so deducted is stated to be as accurate as the gross value obtained by means of the bomb—*i.e.*, within 20 calories per kilo.

"This method of calculation was also found to be applicable to cokes of which a series of 22 samples was examined by the author, the values of N corresponding to 1, 1·5, 2·2, 3, 4, 5, and 6 per cent. of volatile matter in the cokes free from moisture, and ash being 5, 4, 3, 2·5, 2·1, 1·8, and 1·5 respectively."

The methods available for the determination of the water equivalent of the bomb calorimeter have been given in Chapter VI.; in ordinary laboratories the most satisfactory is that in which a known weight of a pure substance, the calorific value of which has been accurately determined, is burnt under conditions similar to those which prevail in actual practice.

We generally make several determinations of the water equivalent, using pure benzoic acid as the combustible substance; and then another set of determinations, using pure cane sugar.

The average figure of the whole of the determinations is taken as the water equivalent. The following results were obtained using 2,500 grammes of water in the calorimeter vessel, the method of working being as described on p. 251 :—

3,193
3,198
3,192
3,194 } Using about 1·5 grammes of cane sugar.
3,200
3,200 } Using about 1 gramme of benzoic acid.

The average figure = 3,196.

The following determinations of the calorific value of benzoic acid were made, using the above figure, and the results obtained for the calorific value of 1 gramme of benzoic acid were :—

6,330
6,277
6,320 } Average = 6,309 calories per gramme.

The most recent determinations give the calorific value as 6,325 calories per gramme. The difference, it will be observed, is about 0·25 per cent., and this may be regarded as within the limits of accuracy obtainable.

In another case the total water equivalent determined by means of benzoic acid was found to be 2,854, and this figure when used for the determination of the calorific value of cane sugar gave 3,966 calories per gramme. This, again, is within 0·3 per cent. of the latest figure given for cane sugar (3,954).

Naphthalene is sometimes used for the determination of the water equivalent, but there appears to be some uncertainty as to its calorific value ; the results obtained by different experimenters do not agree as well as those obtained with benzoic acid and cane sugar.

The following figures show this :—

Benzoic Acid.	Cane Sugar.	Naphthalene.	
6,345	. .	9,688	Berthelot & Recoura.
6,322	. .	9,696	Berthelot & Louginine.
. .	3,962	9,718	Berthelot & Vielle.
6,322	3,955	9,628	Stohmann.
6,355	3,988	9,668	Fischer & Wrede (1904).
6,328	3,954	. .	,, ,, (1908).

The differences in the case of naphthalene have been ascribed by some to possible differences in molecular structure; it will be remembered that the calorific values of the three allotropic modifications of carbon (amorphous carbon, graphite, and diamond) are dissimilar.

The mean of two determinations of naphthalene, using the water equivalent of 3,196, was 9,627, the figures obtained being (*a*) 9,623, (*b*) 9,630.

The main points to be observed when dealing with naphthalene or benzoic acid is to *melt* about the weight required for the determination in a weighed 000 crucible and allow to cool, covered in a good desiccator. When cold the weight is taken, and the crucible is then transferred to the bomb.

The cotton thread is allowed to rest on the surface of the substance, and the determination is then performed, as already described.

If the naphthalene is not melted, or is in a compressed condition, the ensuing combustion is so violent that particles are thrown on to the cold walls of the bomb, and fail to burn completely.

In the case of benzoic acid the crystals are so extremely light and feathery that it is not possible to obtain the required weight in the small crucible unless the melting is resorted to. Cane sugar should be well powdered and dried for a short time at a temperature of 100° C. It is then placed in a well-stoppered weighing tube, and about 1·5 grammes weighed out as required.

In addition to the above substances we have used cellulose, the calorific value of which is 4,209 calories per gramme; inasmuch as this absorbs water very rapidly, it is necessary to dry thoroughly and to protect it from the atmosphere during cooling and weighing.

All of the above pure materials are eminently suitable for calorimetric work, as they are free from nitrogen and sulphur,* and only give carbon dioxide and water as final products. Their heats of combustion, moreover, have been well determined. We prefer benzoic acid, as there is a very close agreement as to its calorific value between different workers, and it is readily obtained pure.

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* A small amount of nitric acid is produced from the nitrogen of the air present in the bomb; this should be determined, and the number of calories to which it is equivalent deducted from the result obtained.

The following is an example of the determination of the water equivalent by means of cane sugar :—

Wt. of cane sugar = 1·4936 grms.
,, water in calorimeter = 2500 grms.

17·840
17·838
17·836 $v = 0·0025$
17·832 $\theta_0 = 17·835$
17·830 $t_0 = 17·830$

19·450
19·820 $n = 6$
19·870
19·870 $\Sigma_1^{n-1} t = 99·072$
19·862
19·854 $t_n = 19·854$

19·844
19·833 $v_1 = 0·010$
19·824 $\theta_n = 19·829$
19·814

Nitric acid produced is equivalent to 3·4 c.c. $\frac{N}{10}$ Na_2CO_3
1·45

580
435

4·930 cal. = 5 calories.

Correction for cotton = 8 ,,

Heat produced other than that from the sugar = 13 ,,

19·854
17·830
Rise to be corrected = 2·024° C.
Σ_Δ = 0·056
Corrected rise = 2·080

Taking 3954 as the calorific value of cane sugar,
Then 1·4936 × 3954 = number of calories due to sugar.
= 5906 calories due to sugar.
= 13 ,, ,, cotton + HNO_3.

5919 = *Total calories introduced into the bomb.*

Rise in temperature = 2·080° C.
2·080 × 2500 = *number of calories imparted to the water.*
= 5200.

Now the difference between these two figures gives the number of calories required to warm the apparatus, 2·080° C., and equals (5,919 — 5,200) = 719 calories, and $\frac{719}{2,080}$ = water equivalent = 346 *grammes of water.* Hence the total water equivalent of the apparatus = 2,846.

The limits of accuracy obtainable in fuel calorimetry have been most ably discussed by Mr. G. N. Huntly in a paper read before the London section of the Society of Chemical Industry.*

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* *Journ. Soc. Chem. Ind.*, vol. xxix., p. 921, 1910.

With his conclusions we entirely agree. They are briefly—" (1) The limit of accuracy in the comparison of the heating values of fuels is from 0·1 to 0·3 per cent., and this can only be reached after a most careful study of the thermometer and calorimeter and the application of numerous corrections.

" (2) If the small corrections are neglected, the errors may amount to from 1 to 2 per cent.

" (3) The heats of combustion of the standard substances used for the determination of the water equivalent are not certain to within 0·5 per cent.

" (4) The errors due to hand sampling cannot be reduced with certainty below 0·5 per cent., and may easily amount to 1·5 to 2·0 per cent.

" Hence, so far as coal is concerned, it is at present more important to devise means for reducing the errors of sampling than to increase the accuracy of the calorimetric determination."

Tables XXXVI. and XXXVII. show the agreement found by Gray and Robertson and Brame and Cowan respectively between various types of calorimeter, and also the values calculated by means of modifications of Dulong's formula. They represent a great amount of useful work, and show that a good agreement with the results of the bomb cannot be expected of instruments of other types (*cf.* pp. 268-9).

In the preceding chapters we have given an account of what we believe to be the most useful or widely adopted methods of examining fuel of various kinds, although, as we stated at the beginning, we do not by any means approve of all the methods described. We have tried to avoid ambiguity in such cases, and to express clearly our reasons for disapproval or qualified approval. It must be understood that methods and apparatus, which one would not be justified in using now, at least in a country where all the resources of civilisation are available, in many cases represent honest attempts which have been of use in their day, and are still of use when no others can be adopted.

The test of laboratory methods cannot in all cases be relied upon to give infallible indications of the probable behaviour of materials on a large scale. Apart from any questions of sampling, which can to a certain extent be solved, and which disappear when the materials, the subject of a long contract, are regularly examined by reason of the compensating effect of errors of opposite sign, the conditions of use frequently cannot be similated on a small scale. When this is the case the laboratory result may

TABLE XXXVI.—SUMMARY OF CALORIMETER RESULTS (*Brame and Cowan*).

Coal.	Lewis Thompson.	Wm. Thomson.	Fischer.	Mahler.	Calorific Value. Calculated.
A. Mean,	8,418 (8)	8,284	8,139	8,629 (3)	8,567
Highest,	8,602	8,490	8,172·5	8,639	
Lowest,	8,082	8,129	8,090	8,613	
Per cent. error,	6·4	4·4	1·0	0·3	
B. Mean,	7,235 (7)	7,178	7,509	7,713 (3)	7,527
Highest,	7,436	7,303·5	7,561	7,727	
Lowest,	7,029	7,090·5	7,465·5	7,706	
Per cent. error,	5·8	3·0	1·3	0·27	
C. Mean,	8,331	8,324 (7)	8,243	8,617 (3)	8,425
Highest,	8,442·5	8,425	8,287·5	8,631	
Lowest,	8,173	8,162	8,187	8,606	
Per cent. error,	3·1	3·2	1·2	0·3	
D. Mean,	8,144	8,233	8,049·7	8,394·5 (3)	8,241
Highest,	8,250	8,304	8,087·5	8,402·5	
Lowest,	8,063	8,156	8,007·5	8,389	
Per cent. error,	2·3	1·8	1·0	0·16	
E. Mean,	8,178	7,882 (8)	7,627	8,026·5 (3)	7,638
Highest,	8,316	7,997	7,648	8,037	
Lowest,	7,997	7,755	7,598	8,018	
Per cent. error,	3·9	3·1	0·6	0·24	

Figures in brackets show number of experiments from which the mean was obtained. When no figures are given the number of experiments was six.

Formula for calculated values: $Q = \frac{1}{100}\left[8{,}140\,C + 34{,}500\left(\frac{H - (O + N) - 1}{8}\right) + 2{,}220\,S\right].$

TABLE XXXVII.—COMPARISON OF RESULTS OBTAINED FROM EXAMINATION OF TWELVE SAMPLES OF COAL IN WHICH THE CARBON RANGED FROM 62·55 TO 85·70 PER CENT., AND THE FIXED CARBON FROM 49·96 TO 88·44 PER CENT. (*Gray and Robertson*).

	CALORIFIC VALUES TO LIQUID WATER.											
Bomb,	6,133	6,439	6,708	6,392	7,099	7,270	7,340	7,392	7,509	7,527	7,801	7,912
Calculated,	6,007	6,354	6,731	6,804	7,003	7,132	7,341	7,246	7,530	7,592	7,785	7,887
Wm. Thomson,	5,989	6,352	6,662	6,658	6,965	7,134	7,223	7,288	7,419	7,308	7,699	7,700
Lewis Thompson,	5,945	6,380	6,560	6,520	6,775	6,958	6,790	6,940	6,880	6,910	7,255	6,880
	DIFFERENCES FROM BOMB RESULTS — PER CENT.											
Calculated,	−2·0	−1·3	+0·3	+0·2	−1·3	−1·9	+0·0	−2·0	+0·3	+0·9	−0·2	−0·3
Wm. Thomson,	−2·3	−1·3	−0·7	−2·0	−1·9	−1·9	−1·4	−1·4	−1·2	−2·9	−1·3	−2·7
WM. THOMSON (USING W.E. CALCULATED FROM RESULTS OF COMBUSTION OF COAL).												
Difference from bomb, %,	−1·1	−0·1	+0·5	−0·7	−0·6	−0·6	−0·3	−0·2	+0·4	−1·8	−0·0	..
Lewis Thompson,	−3·1	−0·9	−2·2	−4·0	−4·6	−4·3	−7·5	−6·1	−8·4	−8·2	−7·0	−13·0

Formula for calculating values: $C.V. = \frac{1}{100}\left[8{,}140\,C + 34{,}500\left(H - \frac{O + N - 1}{8}\right) + 2{,}220\,S\right]$

either indicate an ideal state of affairs, to which it should be the endeavour of the works man to approximate, or may enable an anticipation of the behaviour of the material in practice to be made with a strong *a priori* probability of correctness. In yet a third and lower sense, it may be useful as recording a combination of properties belonging to a material which in practice is found to behave in a certain way, and may thus serve as an empirical precedent for predicting the similar behaviour in practice of materials of similar chemical and physical properties.

It is better to make an experiment on a truck-load than on a ship-load; it is still better to be able to get a good idea of the probable behaviour of a fuel before even a truck-load is ordered, and to be able to choose the most promising of several different fuels before placing even this small order. Besides this, a regular physico-chemical examination of deliveries in a long contract furnishes an equitable basis for payment, and avoids many differences between buyer and seller which are equally vexatious to both, and which may be due rather to the unskilful use of fuel than to any deficiency in quality of the fuel itself. The check on boiler-house practice afforded by systematic examination of fuel is, we know, appreciated by some very large users of fuel who find that their steam-raising results, when everything is going well, vary in very much the same manner as the laboratory tests.

APPENDIX.

Multipliers for Conversion.

From	To	Multiplier.	Logarithms.
Cubic feet,	Litres,	28·317	1·45204
Cubic feet of moist gas per ton, at 60° F. and 30″,	Litres of dry gas per kilo. at 0° C. and 760 mm.,	0·0260	$\bar{2}$·41475
Values per cubic foot at 60° F. and 30″ bar (moist gas).	Values per litre at 0° C. and 760 mm.,	0·03788	$\bar{2}$·57836
Values at 60° F. and 30″ (moist gas),	Values at 0° C. and 760 mm. (dry gas),	1·0735	0·03040
Pounds,	Kilogrammes,	0·4536	$\bar{1}$·65667
Tons,	Do.,	1016·0	3·00689
British Thermal Units,	Calories,	0·2520	0·40143
Litres,	Cubic feet,	0·03531	$\bar{2}$·54796
Litres of dry gas per kilo. at 0° C. and 760 mm.	Cubic feet per ton of moist gas at 60° F. and 30″	38·48	1·58525
Values per litre at 0° C. and 760 mm.,	Values per cubic foot at 60° F. and 30″ bar.,	26·40	1·42164
Values at 0° C. and 760 mm. (dry gas),	Values at 60° F. and 30″ (moist gas),	0·9324	$\bar{1}$·96960
Kilogrammes,	Pounds,	2·2046	0·34333
Do.,	Tons,	0·00098	$\bar{4}$·99310
Calories,	British Thermal Units,	3·968	0·59857

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