DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 36

INDUSTRIAL GAS CALORIMETRY

BY

C. W. WAIDNER, Physicist

and

E. F. MUELLER, Assistant Physicist

Bureau of Standards

[MARCH 1, 1914]

WASHINGTON
GOVERNMENT PRINTING OFFICE
1914

ADDITIONAL COPIES
OF THIS PUBLICATION MAY BE PROCURED FROM
THE SUPERINTENDENT OF DOCUMENTS
GOVERNMENT PRINTING OFFICE
WASHINGTON, D. C.
AT
40 CENTS PER COPY

▽

INDUSTRIAL GAS CALORIMETRY

C. W. Waidner and E. F. Mueller

CONTENTS

	Page
I. Object and scope of the investigation	5
II. Laboratory equipment	7
III. Heat units and heats of combustion	9
IV. Types of calorimeters	15
V. Principles of flow calorimetry and determination of total and net heating values	17
VI. Measurement of gas volumes—Investigation of laboratory type of gas meters	23
1. Reduction to standard pressure and temperature	23
2. Construction and mode of operation of meters	24
3. Preparation of the meter for use	26
4. Method of use	27
5. Investigation of sources of error	28
(*a*) Method used	28
(*b*) Leveling	29
(*c*) Adjustment of water level	29
(*d*) Temperature, humidity, and pressure	29
(*e*) Variation of calibration with rate	31
(*f*) Reproducibility of the calibration	32
(*g*) Fractional revolutions	33
(*h*) Effect of resistance to rotation	34
6. Absolute calibration	35
(*a*) Meter prover	35
(*b*) Aspirator bottle	35
(*c*) Standardized bottles	38
(7) Summary of meter tests	39
VII. Factors affecting heating value determinations with flow calorimeters	41
1. Completeness of combustion	41
2. Temperature measurements	43
3. Heat losses from calorimeter	49
(*a*) Efficiency of calorimeter	49
(*b*) Surface losses	52
(*c*) Position of burner in calorimeter and use of radiation shields on burner	57

VII. Factors affecting heating value determinations with flow calorimeters—Continued

Page

3. Heat losses from calorimeter—Continued
(*d*) Conduction down stem of burner 61
(*e*) Heat carried off by products of combustion 61
Saturation of entering air; of gas; of products 62
Volume of entering air and of products 63
Normal rate of gas consumption; ratio of air to gas at the normal rate 69
(*f*) Effect of atmospheric humidity 72
4. Temperature of inlet water 78
5. Constancy of flow of water and of gas—Efficiency of gas pressure regulators 81
6. Time required for the attainment of thermal equilibrium in flow calorimeters 83
7. Measurement of water condensed in calorimeter. Net heating value 87
8. Manipulation of change-over device 88
9. Weighing or measuring the water 90
10. Measurement of volume of gas 92
11. Leakage of gas 93
12. Measurement of atmospheric pressure 93
13. Effect of using fresh water in gas meter 95
14. Effect of use of new rubber tubing 96
15. Effect of cooling gas on heating value and on candlepower 97
16. Deterioration in heating value of gas in holder 98
17. Résumé of factors affecting heating value determinations 99

VIII. Comparison of heating values of gases determined with flow calorimeters with those obtained with calorimeters of the Berthelot bomb type 100
1. Apparatus and methods 100
2. Comparisons with natural gas 103
3. Comparisons with hydrogen 106
4. Comparisons with illuminating gas 107

IX. Tests of various gas calorimeters 110
1. Junkers calorimeter (original type) 110
2. Hinman-Junkers calorimeter 113
3. Sargent colorimeter 115
4. Junkers calorimeter (new type) 116
5. Simmance-Abady calorimeter (English type) 119
6. Boys calorimeter 123
7. Simmance-Abady calorimeter (American type) 130
8. Doherty calorimeter 132
9. Parr gas calorimeter 140

X. Summary 148

I. OBJECT AND SCOPE OF THE INVESTIGATION

The first laws and regulations adopted by cities, and later by States, related to the photometric requirements which manufactured gas must fulfill. With the increasing applications of gas to heating and power purposes, and to mantle lighting, the importance of the heating value of the gas began to be realized. It has been estimated that at the present time over 80 per cent of the gas distributed in the United States is applied to the purposes stated above, and perhaps as much as 90 per cent in many cities. The tendency of recent legislation [1] and regulation has therefore been toward the adoption of either a double standard, including both an illuminating value and a heating value standard, or, in many instances, the adoption of a standard heating value alone.

In view, therefore, of the increasing importance of the measurement of the heating values of gases, the object of the present investigation was an experimental study of the leading types of gas calorimeters that are widely used in the gas industries, in order to furnish gas engineers, public-service commissions, and gas inspectors exact information as to the accuracy attainable with the instruments, the sources of error to which they are liable, and the important precautions that should be observed in their use in order to obtain reliable results.

The committee on calorimetry of the American Gas Institute has for several years been conducting a series of valuable tests on gas calorimeters, the results of which are contained in several reports to the institute,[2] and the careful reading of these is recommended to those interested in gas calorimetry. The necessity of the present investigation was urged by J. B. Klumpp, chairman of the committee, and by many other eminent gas engineers, with a view to obtaining independent evidence on the conclusions arrived at by the committee, and with a view to considering some of the problems that could not be taken up by the committee in the time at the disposal of its members. The investigation was also made necessary at this time by the fact that the

[1] A review and discussion of laws and regulations relating to gas will be found in Circular of the Bureau of Standards, No. 32, "Standard regulations for manufactured gas and gas service."

[2] Proc. Am. Gas Institute, **3**, 285, 1908; **4**, 148, 1909; **7**, 65, 1912.

Bureau was being called upon by public-service commissions and others to test calorimeters of various types.

The calorimeters included in this investigation are enumerated in Table 1. All of the calorimeters are of the flow type except the Parr, which is of the comparison type.

TABLE 1

List of Calorimeters Investigated

Calorimeter	Maker
Junkers, original type	Junkers & Co., Dessau, Germany.
Junkers, new type	Do.
Hinman-Junkers	American Meter Co., New York, N. Y.
Sargent	Sargent Steam Meter Co., Chicago, Ill.
Simmance-Abady, English type	Alex. Wright & Co. (Ltd.). Westminster, London, England.
Simmance-Abady, American type	Precision Instrument Co., Detroit, Mich.
Boys	John J. Griffin & Sons, London, England.
Doherty	Improved Equipment Co., New York, N. Y.
Parr	Standard Calorimeter Co., E. Moline, Ill.

With a view to making the results of this investigation available to those who have not had a special technical training, the matter is presented in somewhat greater detail than would be strictly necessary for the scientific reader. However, in order not to unduly extend the length of this report, only the conclusions, based on a vast amount of experimental data, have in many instances been given, and only sufficient data have been given here and there throughout the report to familiarize the reader with the experimental methods employed in investigating the various questions that have been considered.

The methods of operation which this and other investigations have shown to be suitable for the various calorimeters are given in the section on "Measurement of heating values," in Bureau of Standards Circular No. 48, in the form of detailed operating directions. The section referred to also contains other matters of interest in connection with the equipment of a calorimetric laboratory. Tables to be used in connection with heating-value determinations are also included in the circular.

The more important conclusions of this investigation are briefly summarized on pages 39 to 40, and 148 to 150.

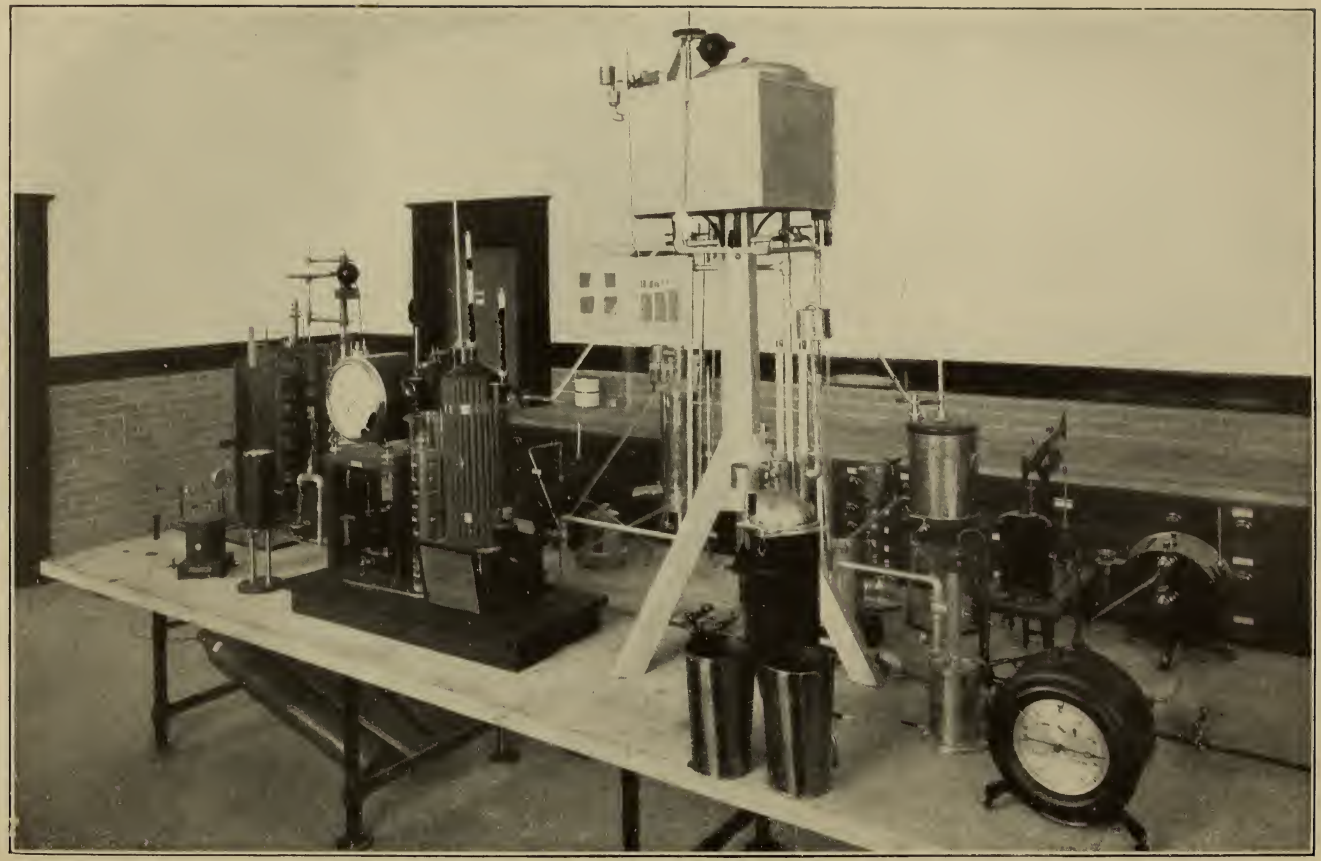


Fig. 1.—*View of calorimetric laboratory*

II. LABORATORY [3] EQUIPMENT

GAS SUPPLY

There was available for this investigation a 5 cubic-foot meter prover, which was used as a gas tank for drawing from the laboratory gas mains samples of the gas to be used in testing the calorimeters and similarly for holding the samples of natural gas and of hydrogen used in intercomparing the different calorimeters.

The gas connections used will be understood by reference to Fig. 2. Gas from the mains passes through the pressure regulator A, the meter B, the three-way stopcock C, another regulator D, and to the burner in the calorimeter. An unlimited supply of gas, of approximately the same heating value as that in the holder, was thus available for bringing the calorimeter to equilibrium,

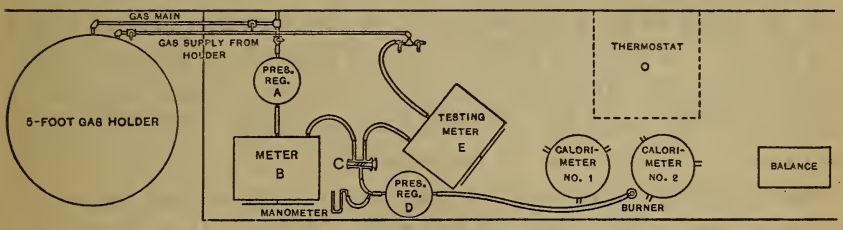


Fig. 2.—*Diagram of gas connections*

adjusting the rate of gas consumption, etc. When a test was to be made the three-way stopcock was turned, causing the gas to flow from the gas holder through the testing meter E to the burner. With this arrangement as many as 12 separate determinations of heating value could be made with one holder full of gas, and the conditions between tests could be varied as desired. Further, during such a series of determinations, only the amount of gas used in the tests was passed through the testing meter, thereby diminishing the possibility of change in the water level in the meter during the experiments. In any such series of determinations the last tests were made under conditions identical with the first tests, so as to determine whether any changes had taken place during the series, as, for example, a change in the heating value of the gas drawn from the holder.

[3] A general view of the laboratory is shown in Fig. 1.

Calorimeters which were to be compared were set up so that the gas supplied through the system described could be burned in the two alternately, giving the most favorable conditions for determining any difference in heating values as measured with the two calorimeters.

WATER SUPPLY

At some distance above the table in Fig. 1 is shown a thermostatically controlled water bath from which water at constant temperature was delivered to the calorimeters.

The principle of action of this thermostat is briefly as follows: Water from the house piping is delivered into the thermostat slightly in excess of that drawn from it by the calorimeters, the excess being passed to drain through an overflow. Within the thermostat is a helical coil filled with an expansible liquid which, acting on a mercury U gauge, makes and breaks an electric circuit in which is an electromagnet, on the movable arm of which is a bucket. There is a second delivery pipe which discharges into the thermostat a stream of hot water in excess of that required to bring the thermostat to the desired temperature. When the temperature of the water in the thermostat attains that for which the mercury contact is set the electromagnet is operated and the bucket is moved under the stream of hot water, which is thus diverted to drain. The supply of hot water being cut off, the temperature falls, the electric circuit is interrupted, hot water is again delivered into the thermostat, etc.

When the temperature of the water in the house piping was already above that to be delivered by the thermostat, which was the case in summer, the hot-water supply was replaced by a cooled-water supply.

To insure thorough mixing of the two streams of water delivered into the top of the thermostat, these streams were delivered into a brass tube, extending from a short distance below the upper surface of the water nearly to the bottom, in which tube was mounted a motor-driven stirrer of the propeller type.

This thermostat would deliver to the calorimeters water the temperature of which was constant to 0°.01 or 0°.02 F for long periods. The importance of using water at constant inlet temperature will be recognized when it is remembered that a change

of temperature of the inlet water does not make itself manifest at the calorimeter outlet until some time after the change has taken place, so that considerable error may result if the temperature of the inlet water varies much during the progress of a heating-value test, although this error may be diminished by proper procedure. (See p. 45.)

OTHER EQUIPMENT

Other items of equipment were a Rueprecht equal-arm balance; flow calorimeters enumerated on page 6; experimental wet meters of the American Meter Co., Elster, Sargent, Griffin, and Alexander Wright makes; a one-tenth cubic foot bottle; several complete calorimeters of the Berthelot bomb type with all accessories, such as calorimetric resistance thermometers, special resistance bridges, etc.; an Assmann aspiration psychrometer; a Fuess standard barometer; several wet pressure regulators of different types; weighing buckets; graduates; thermometers; gas tanks; etc. The laboratory table with stone top was provided with gas, compressed air, vacuum, hot-water, cold-water, and ice-water outlets, drain connections, and electric wiring.

III. HEAT UNITS AND HEATS OF COMBUSTION

HEAT UNITS

A quantity of heat is usually measured by the change in temperature which it can produce in a known mass of water. The heat unit is, therefore, defined as the quantity of heat required to raise the temperature of unit mass of water one degree. As the specific heat of water is not a constant but varies slightly with the temperature, it is further necessary, in precise scientific work, to specify the temperature of the water. Although the heat unit has not been defined by any international congress, it has become the general custom to express quantities of heat in terms of water at 15° C (59° F). More recently a preference has been shown, for a number of reasons, for a calorie defined in terms of the capacity for heat of water at 20° C, or even at a higher temperature. The difference between the 15° and the 20° calorie is negligible for the purposes of industrial gas calorimetry and the former has been retained in the present report.

The units in which the heating values (or heats of combustion) of fuels, foods, explosives, etc., are expressed are: (*a*) the (small) *calorie;* (*b*) the (large) *Calorie;* and (*c*) the *British thermal unit*, designated briefly Btu.

The calorie is the quantity of heat required to raise the temperature of 1 gram of water 1° at 15° C.

The Calorie is the quantity of heat required to raise the temperature of 1 kilogram of water 1° at 15° C.

On the same basis the British thermal unit is the quantity of heat required to raise the temperature of 1 pound of water 1° at 59° F.

For converting quantities of heat expressed in terms of any one of the heat units defined above to quantities of heat expressed in terms of either of the other two heat units, the following are the conversion factors:

1 Calorie = 1000 calories;

1 British thermal unit = 252.0 calories.

For the order of accuracy required, or readily attainable, in nearly all engineering or industrial tests, the variation of the specific heat of water in the range of temperatures within which calorimetric experiments are conducted is so small that it may be neglected. For example, the amount of heat required to raise the temperature of a given mass of water 1 degree at 35° C (95° F) is about 1 part in 500 (0.2 per cent) smaller than that required at 15° C (59° F).

The specific heat of water has been the subject of elaborate investigations by numerous experimenters, but there is considerable discrepancy between the various published values. Table 2 is given to show the order of magnitude of the variation of the specific heat of water with temperature. The values given were obtained by inspection of the data summarized by Börnstein and Scheel in the Landolt-Börnstein-Roth Physikalisch-Chemische Tabellen, Table No. 171, page 760, and are sufficiently accurate for the purposes of industrial gas calorimetry.

As tap water is used for measurements with flow calorimeters, it is of interest to estimate what degree of impurity is of significance in such measurements. Examination of published data on the specific heats and the densities of dilute solutions shows that for the class of soluble matter likely to occur in city water supplies

an increase of 1 per cent in the density will cause a diminution of the specific heat of about 2 per cent. Hence, if the error in the calorimetric measurement due to impurities of this kind in the tap water is not to exceed 0.1 per cent, the density of the tap water should not differ from that of pure water by more than 0.05 per cent if the water is weighed in the calorimetric test, or by more than 0.1 per cent if the water is measured volumetrically. The error in a calorimetric measurement, due to the effect of impurities on the specific heat of water, is less if the water is measured than if it is weighed, because the volume specific heats of the dilute solutions here considered vary less rapidly with concentration than do the mass specific heats. As measurements of specific heats present great experimental difficulties, while density determinations to the required accuracy are readily made, a criterion of the purity and therefore of the specific heat of the water is most simply obtained from density measurements.

TABLE 2

Specific Heat of Water at Various Temperatures in Terms of the Specific Heat at 15° C Taken as Unity

Temperature	Specific heat
°C	
5	1.004
10	1.002
15	1.000
20	.999
25	.998
30	.998
35	.998

The specific heat of the tap water used in the present series of experiments differed from that of pure water by much less than 0.1 per cent, as shown both by density measurements and by determinations of the specific heat in other calorimetric researches.

HEATS OF COMBUSTION

In formulating a precise definition of the heat of combustion of a substance, it is necessary to specify the following:

(*a*) What compounds are to be formed from the elements which the substance contains when the substance combines with oxygen.

(*b*) The quantity and the initial state (solid, liquid, or gaseous) of the substance. If the substance be a gas, the quantity contained in a given volume will depend on the temperature and pressure of the contained gas. Hence, in order that the term "heat of combustion of a gas" may have a definite meaning, the volume of the gas must be referred to some standard temperature and pressure. In scientific work the volume of the gas is reduced to what it would be at 0° C and under 760 mm pressure (standard gravity). In industrial and engineering work, where water vapor enters into the composition of the gas, it is also necessary to specify the water vapor content of the gas. In engineering tests and for the purpose of the industrial testing and measurement of gases the standard temperature and pressure almost invariably used in the United States are 60° F and 30 inches of mercury, and the gas, for purposes of testing, is saturated with water vapor.

(*c*) The number of heat units produced by the combustion of the given quantity.

(*d*) The conditions (constant pressure or constant volume) under which combustion takes place.

(*e*) The initial temperature of the substance and oxygen (or air) and the final temperature of the products. It is not sufficient to specify merely that these temperatures shall all be equal, since, on account of the difference in the heat capacity of the substance plus oxygen and that of the products, the amount of heat produced by the combustion will depend, to a small extent, on the temperature chosen.

(*f*) The pressure, if the combustion takes place at constant pressure. This is for reasons similar to these given for (*e*), above. Naturally, in defining the heat of combustion the initial temperature chosen would be that for which the heat unit is defined and the constant pressure chosen would be the standard atmospheric pressure.

(*g*) The states, solid, liquid, or gaseous, to which the various products are reduced.

The following general definition is formulated in accordance with the requirements outlined above:

The heat of combustion, at constant pressure, of a gas containing only the elements, or compounds of the elements, carbon, hydro-

gen, oxygen, and nitrogen, is the number of heat units produced by the combustion of unit quantity of the gas initially at a specified temperature and at standard atmospheric pressure, with oxygen at the same temperature and pressure, with formation of gaseous carbon dioxide and nitrogen and liquid water, all cooled to the initial temperature and at standard atmospheric pressure; unit quantity of the gas being the quantity which would occupy unit volume at the standard temperature and standard pressure chosen for gas measurement.

A definition of this type is, however, too complicated for engineering or industrial use. A simpler and quite satisfactory definition can be formulated by omitting reference to (*a*), the omission being more or less supplied by the use of the term "combustion" and by explicitly omitting (*e*) and (*f*), so that, in such a definition, no account is taken of the temperature or pressure coefficients of the reactions. In testing complex mixtures, such as illuminating gas, it is difficult to calculate the coefficients, and in any case no significant difference would be introduced by neglecting them.

For the reasons outlined above, the following definitions are sufficiently precise for engineering and industrial use:

The *total heating value* of a gas, expressed in the English system of units, is the number of British thermal units produced by the combustion, at constant pressure, of the amount of the gas which would occupy a volume of 1 cubic foot at a temperature of 60° F, if saturated with water vapor, and under a pressure equivalent to that of 30 inches of mercury at 32° F and under standard gravity, with air of the same temperature and pressure as the gas, when the products of combustion are cooled to the initial temperature of gas and air and when the water formed by combustion is condensed to the liquid state.[4]

[4] The definition of the total heating value of gas adopted by the American Gas Institute (Proc., 3, p. 383; 1908) is as follows: "The heating value of a gas is the total heating effect produced by the complete combustion of a unit volume of the gas, measured at a temperature of 60° F and a pressure of 30 inches of mercury, with air of the same temperature and pressure, the products of combustion also being brought to this temperature." This definition does not call attention to the fact that the condition of saturation with water vapor of the gas must be defined. The pressure of 30 inches of mercury is not definite unless the temperature of the mercury be also specified. The definition does not distinguish between total and net heating value, since it fails to specify whether the water formed in combustion is to be in the form of liquid or of vapor, when the products are cooled to the initial temperature.

The *net heating value* of a gas, expressed in the English system of units, is the number of British thermal units produced by the combustion, at constant pressure, of the amount of the gas which would occupy a volume of 1 cubic foot at a temperature of 60° F, if saturated with water vapor and under a pressure equivalent to that of 30 inches of mercury at 32° F and under standard gravity, with air of the same temperature and pressure as the gas, when the products of combustion are cooled to the initial temperature of gas and air and the water formed in combustion remains in the state of vapor.

According to the above definitions the net heating value is less than the total heating value by an amount of heat equal to the latent heat of vaporization, at the initial temperature of the gas and air, of the water formed by the combustion of the gas.

For most calorimetric calculations the heat of vaporization of water may be taken as being equal to 580 calories per gram, corresponding to 2.3 Btu per cc (graduates are almost invariably calibrated in cc).

In addition to the terms "total heating value" and "net heating value," the term "*observed heating value*" will be used, as a matter of convenience, in discussing the experimental data. The observed heating value for a flow calorimeter will be understood to be the value obtained by multiplying the mass of water which flowed through the calorimeter during the test by the corrected rise in temperature of the water, and dividing by the volume (referred to the standard conditions of 60° F and 30 inches) of gas burned.

It has been the general practice to regard the observed heating value as identical with the gross (total) heating value. This practice is not permissible if an accuracy better than 2 or 3 per cent is required, since even with a perfect flow calorimeter these two heating values would necessarily differ by 2 per cent or more under certain atmospheric conditions (e. g., 10 per cent humidity and 90° F; see Table 19), while for some of the calorimeters tested the difference might amount to about 4 per cent.

In view of the fact that the term "gross heating value" was intended to mean total heating value, but has generally been

applied to the observed heating value as well, it seems desirable to discontinue the use of the term "gross heating value." If the term "total heating value" is adopted, strict consistency of nomenclature might require the discontinuance of the use of the term "net heating value" and the use of "partial heating value" in its stead. This practice has not been followed in the present report.

The heating values found with well-designed flow calorimeters (after the necessary corrections are applied for loss of heat to surroundings, heat carried off in products, etc.) are the total heating value and the net heating value defined above. The heat of combustion directly found with calorimeters of the Berthelot bomb type is the total heat of combustion under the condition of constant volume. The difference between the heat of combustion at constant pressure and at constant volume is due to the work done by the external pressure on the products of combustion, and is measured by the product of this pressure and the change in volume of the gases taking part in the reactions. If the change in volume due to the reaction is known or if the composition of the gas is known, so that the change in volume may be calculated, the heat of combustion expressed under either condition may be reduced to the other.

IV. TYPES OF CALORIMETERS

Many types of calorimeters have been suggested and used to measure heats of combustion of gases.

(*a*) In the Berthelot bomb type the combustion takes place at constant volume within a bomb in the presence of sufficient oxygen to insure complete combustion. This type of calorimeter gives the total heat of combustion at constant volume.

(*b*) In the Regnault and Julius Thomsen types the gas is burned in a combustion chamber within the calorimeter and the products of combustion are caused to give up their heat by being passed through a worm immersed in the water of the calorimeter.

(*c*) In the comparison type, such as the Parr gas calorimeter, the rise in temperature produced in a calorimeter by the combustion of a given volume of the gas is compared with the rise in temperature produced in a similar calorimeter by the combustion of a

known volume of a gas the heat of combustion of which is known. In a restricted sense the Strache calorimeter is an instrument of this type.

(*d*) The water-flow type is utilized most frequently for the calorimetry of gases and is exemplified in the calorimeters listed on page 6, with the exception of the Parr calorimeter. The principles of the flow calorimeter are discussed in the following section:

(*e*) A large number of gas calorimeters have been devised, the operation of which depends upon the indications of some thermometric device, heated by gas burned at a constant rate as controlled by a pressure regulator or other regulating mechanism. The thermometric device may be thermoelectric or may depend upon the expansion of a solid, of a liquid, or of a gas. The Fery calorimeter, the Fahrenheim, the Smith, and the Sarco recording calorimeters and the Simmance-Abady calor-graph are calorimeters of this type. In another class of calorimeters a definite quantity of gas is burned in the apparatus and the heating value of the gas deduced from the change of temperature of a mass of material subjected to the action of the flame. The Graefe and the Raupp calorimeters are of this type. The indications of these calorimeters are arbitrary and they must be calibrated by comparison with a standard calorimeter. Since the products of combustion escape from such calorimeters at relatively high temperatures, these instruments are usually calibrated for indicating or recording net heating values.

In all of the types described, except (*a*), the combustion takes place under the condition of constant pressure. Calorimeters of types (*b*), (*c*), and (*d*) are used to measure the total heat of combustion at constant pressure, and when suitably constructed some of them may be used to measure the net heat of combustion at constant pressure. Calorimeters of type (*d*) have been used in connection with recording devices to obtain continuous records of total heating values.

The reader will find descriptions of numerous calorimeters in the publications of Immenkötter [5] and of Coste.[6]

---

[5] Über Heizwerthbestimmungen mit besonderer Berücksichtigung gasförmiger und flüssiger Brennstoffe, published by R. Oldenbourg, Munich and Berlin.

[6] The Calorific Power of Gas, published by Chas. Griffin & Co. (Ltd.), London.

V. PRINCIPLES OF FLOW CALORIMETRY AND DETERMINATION OF TOTAL AND NET HEATING VALUES

In flow calorimeters the heat to be measured is imparted to a stream of water, the mass of water flowing through the calorimeter during the time that a known mass or volume of the combustible is burned within the calorimeter and the resulting change in temperature of the water, furnishing the data necessary for calculating the heat imparted to the water. There are always, however, some losses of heat from the calorimeter, the magnitude of which must be determined in order that suitable corrections may be applied to the observed heating value, if such losses are large enough to be of significance for the accuracy that is sought.

The details of construction of various makes of flow calorimeters are shown in the illustrations and sectional drawings included in this report. The gas, the heating value of which is to be determined, is measured with a suitable wet meter, and is burned at a constant rate in a suitable burner within a nearly closed chamber called the combustion chamber. The air necessary to support the combustion enters the combustion chamber through the open bottom of the calorimeter, the circulation through the calorimeter being induced by the heated products of combustion. Under some conditions (e. g., open damper, small rate of gas consumption) the air drawn through the calorimeter is very considerably in excess of that required for combustion, while at high rates of combustion the air supply may be insufficient to insure complete combustion.

The heated products [7] pass up through the combustion chamber, which is surrounded by the flowing water, then downward through tubes or spaces also water cooled, and finally are discharged into the atmosphere through an outlet in which a damper, by which the amount of air drawn through the calorimeter may be controlled, is usually placed. The heated gaseous products are thus made to impart to the water flowing through the calorimeter nearly all the heat resulting from combustion.

[7] As a matter of convenience the gases discharged from the calorimeter, which include practically all of the products of combustion except the water condensed in the calorimeter, as well as the nitrogen and excess oxygen from the entering air, will be referred to as the products of combustion, or often simply as the products.

The temperature of the water entering and leaving the calorimeter is measured by the inlet and outlet water thermometers, respectively. A mixing device should be provided to thoroughly mix the heated water before it reaches the bulb of the outlet-water thermometer in order that this thermometer shall indicate the true mean temperature of the effluent water. The water flows through the calorimeter under a pressure determined by the difference in level of the inlet and outlet overflow wiers. The rate of flow of water, and hence its rise of temperature, may be varied by a suitable valve.

The determination of the heating value of a gas by means of a flow calorimeter was carried out as follows: Gas was burned at the proper rate (as measured by the gas meter) and with proper air supply (controlled by the damper) in a suitable burner placed within the combustion chamber of the calorimeter; the rate of flow of water through the calorimeter was so adjusted (by the valve) that the rise of temperature of the water was the desired amount (usually 15° to 20° F); the temperature of the water was so regulated that it entered the calorimeter at approximately room temperature; after the gas had been burning long enough for a condition of thermal equilibrium to be set up in the calorimeter, observations were begun by reading (*a*) pressure, temperature, and humidity of air; (*b*) temperature of products of combustion; (*c*) temperature of gas meter and the gas pressure at meter inlet; (*d*) series of readings of inlet and outlet water thermometers; (*e*) weight or volume of water which flowed through the calorimeter during the combustion of the chosen volume of gas (usually two turns of the one-tenth or one-twelfth cubic foot meter).

Two or three readings of the outlet-water thermometer were taken before the index of the gas meter passed through its zero position; at this instant the change-over device, into which the water discharged from the calorimeter, was shifted to divert the water from drain to measuring vessel. Observations of the readings of the outlet-water thermometer were then made at frequent and regular intervals until the index of the meter had made nearly two complete revolutions (i. e., until $2 \times \frac{1}{10}$ or $2 \times \frac{1}{12}$ cubic feet of gas had been burned). The instant the index of the meter passed

through zero, on completion of its second revolution, the change-over device was shifted, diverting the water from measuring vessel back to drain. One or two more readings of the outlet-water thermometer and one more reading of the inlet-water thermometer were taken and then the water collected was weighed.

The readings of the outlet-water thermometer before and after shifting the change-over device were taken simply to show that steady conditions had been maintained before and after the test.

The barometric pressure was read to enable the volume of gas burned during the experiment, as measured by the meter, to be reduced to standard conditions, and the humidity of the air of the room was determined by a suitable wet and dry bulb psychrometer of the aspiration type to enable the correction to be applied to reduce the observed heating value to the total heating value, as hereinafter explained.

The observations above referred to, all of which may be taken in a few minutes, contain all the data necessary for a single determination of the total heating value of the gas burned in the calorimeter. For calculating the net heating value of the gas the amount of water vapor condensed out of the products of combustion of a known volume (1 cubic foot is sufficient) of the gas was collected and measured in a 25-cc graduate placed under the drip tube at the base of the calorimeter. The collection of this condensate for purposes of measurement should obviously not be started until the gas has been burning in the calorimeter long enough to insure that the inner walls and tubes of the calorimeter have become uniformly wetted and the drainage therefrom has become uniform.

The accuracy with which the various operations incident to the determination of the heating value of a gas can be carried out are considered in detail in later sections. It will probably assist in reading what follows to anticipate some of the experimental results discussed in detail later and consider at this point the various heat losses from one of these flow calorimeters and give an example of the observations necessary and the mode of calculation used to find the corrected total and net heating values of a gas.

Assuming for the present that the type of burner and the air supply are such that the combustion is complete, then, in an efficient calorimeter, all but a small proportion of the heat produced in the combustion chamber is communicated to the water flowing through the calorimeter, and is thus measured by the product of the quantity of water flowing through the calorimeter and the resulting rise in temperature of the water.

The combustion products escape from the calorimeter at a temperature slightly above that of the inlet water, which for the present is assumed to be at room temperature. If the products escape at a higher temperature, they carry off some sensible heat which, however, is rarely as much as 0.1 per cent of the heat measured. These products, however, are saturated or nearly saturated with water vapor at the temperature at which they escape from the calorimeter, and if a large amount of relatively dry air is drawn into the calorimeter, the escaping products will carry off considerable amounts of water vapor taken from the water produced by the combustion; that is, a considerable correction will be necessary to allow for the heat of condensation thus lost from the calorimeter. The magnitude of this correction will evidently depend upon the volume of air taken into the calorimeter, the volume of the products, and the temperatures and degrees of saturation of the entering air and gas and of the escaping products. Hence, it will be seen that the observed heating value for a given sample of gas will depend upon the humidity of the air at the time of the experiment.

Another source of error is the heat interchange between the calorimeter and the room, due to the fact that the average temperature of the surface of the calorimeter differs from that of the room. The heat interchange may conveniently be considered as made up of two parts—(*a*) that due to the excess of the average temperature of the surface above that of the inlet water and (*b*) that due to the difference between inlet water temperature and room temperature.

Suitable corrections were applied to the observed barometric pressure, the readings of the psychrometer thermometers, the gas-meter thermometer, the inlet and outlet water thermometers,

the combustion products thermometer, and to the observed weight of water. However, sufficiently accurate thermometers can be obtained for the psychrometer, the barometer, the gas meter, and the products so that the corrections may be neglected. Sets of weights and balances can also be obtained of such accuracy that their errors are negligible. The only significant correction to the weighings is then the so-called reduction to vacuo (see p. 90), which amounts to about 1 part in 1000 of the weight of water.

If the Btu is defined in terms of water at 60° F and the mean temperature of the water during the test is 90° F, a correction would be required, due to the variation of the specific heat of water, amounting to about 0.2 per cent. In routine gas testing the application of corrections for reduction to vacuo and for variation of the specific heat of water may be omitted, since both corrections are small and, for the usual conditions under which flow calorimeters are used, are of opposite sign and tend to neutralize one another.

The complete data and reductions for the determination of the total and net heating values of a sample of gas are given in Table 3. This is not an exact copy of the laboratory records. All measurements in this investigation were made in the metric system of units (liters, grams, °C). A record form to be used in routine testing may be found in Bureau Circular No. 48.

TABLE 3

Observed Data and Computation for a Determination of Total and Net Heating Values

	Inlet thermometer #5808A	Outlet thermometer #5808C
Gas not burning	=85°46	85°46
Certif. cor.	+04	+06
	85.50	85.52

∴Apply a differential correction of −0°02 to readings of outlet thermometer (*a*)

Temperature controlled by thermostat.

Inlet	Outlet
85.46	103°43
	.50
	—— *b*
	.50
	.46
	.43
	.46
	.43
	.50
	.51
	1 turn→
	.55
	.60
	.53
	.51
	.50
	.60
	—— *b*
	.59
85.46	.51
85.46	103.51
Certif. cor. +.04	+.13
Stem cor. 00	+.11
Differential cor.	−.02
85.50	103°73
	85°50
∴Corrected temp. rise.....	=18°23

(*c*) Products=85°8

Meter =85°6

Gas pressure at meter inlet=1.5 ins. water

(*d*) Gas rate 6.9 cu. ft. per hour, damper closed.

(*e*) Condensed water collected for 7 turns of meter=12.5 cc; condensate per cu. ft. =19.4 cc

Weight of water	6.708 lbs.
Reduction to vacuo	+.007
Cor. to weights	.000
Mass of water	=6.715 lbs.

(*h*) Volume of gas

Meter No. 6312

2 turns of meter	0.2000 cu. ft.
Cal. cor. (0.53% slow)	+.0011
Vol. delivered at 85°6 and 29.75 ins.	0.2011 cu. ft.
∴Vol. at 60° and 30 ins.	=0.1854 cu. ft.

Observed htg. value $= \frac{6.715 \times 18.23}{0.1854} = 660.3$ Btu

(*d*) Correction for atmospheric humidity	+5.0 "
(*i*) Radiation correction	+0.8 "
(*j*) Cor. for var of sp. heat of water (to reduce to 60° F Btu)	−1.3 "
(*k*) ∴Total htg value	=665 Btu.

Obs., htg value	660.3 Btu
(*e*) Cor. for 19.4 cc of condensate	−44.6 "
(*i*) Cor. for radiation	+0.8 "
(*j*) Cor. for sp. heat of water (to reduce to 60° F Btu)	−1.3 "
(*l*) Net heating value	=615 Btu.

(*f*) Barometer

85°6	29.80 ins.
Scale and index	.00
Gravity	−02
Temp.	−14
Cor. bar.	29.64
Gas pres.	.11
Pres. on gas	29.75

(*g*) Psychrometer

Dry bulb	85°6
Wet bulb	69°8
∴Humidity	=45%

EXPLANATORY NOTES TO TABLE 3

(*a*) When no gas was burning the readings of the inlet and outlet water thermometers, corrected by the certificate corrections, would have been equal if no changes had taken place in the thermometers since they were tested and if there had been no heat interchange between the calorimeter and its surroundings. The

VI. MEASUREMENT OF GAS VOLUMES—INVESTIGATION OF LABORATORY TYPE OF GAS METERS

Inasmuch as the measurement of gas volumes enters directly into all tests of the heating values of gases an investigation of the accuracy with which such measurements could be made and of the sources of error affecting them was a necessary preliminary to the investigation of the calorimeters.

1. REDUCTION TO STANDARD PRESSURE AND TEMPERATURE

To make the terms "cubic foot," "liter," etc., of gas definite it is necessary to define not only the volume but also the pressure, temperature, and degree of saturation, with water vapor, of the gas. A measurement of a volume of gas made with any suitable measuring device, at a known pressure, temperature, and degree of saturation, must therefore be reduced to what it would become under some standard conditions of pressure, temperature, and saturation.

---

latter condition was secured in this test by adjusting the inlet water temperature to approximate equality with room temperature. If the inlet water temperature is not extremely constant and approximately equal to room temperature, the intercomparison of the thermometers should be made in a pail of well-stirred water rather than in the calorimeter. The differential correction eliminates the error due to relative changes that have occurred in the thermometers since they were tested and certified.

(*b*) Pointer of meter passes through zero position. Change over device shifted to weighing bucket at instant of first passage through zero and back to drain at instant of third passage through zero, so that water collected for weighing corresponds to gas burned during two turns of meter (0.2 cubic feet, approximately).

(*c*) The temperature of the combustion products should, if the calorimeter is operating properly, be very nearly the same as the inlet-water temperature. It is then not necessary to take it into account in the computations.

(*d*) When this calorimeter is operated with the damper closed and illuminating gas is burned at the rate of about 7 cubic feet per hour, approximately 7 volumes of air are drawn into the calorimeter for each volume of gas burned and 6.6 volumes of combustion products are discharged. The correction for atmospheric humidity can therefore be taken from Table 19, page 77.

(*e*) The condensate was measured in a 25-cc graduate divided into 0.5 cc intervals. The latent heat of vaporization of 1 cc=2.3 Btu at the temperature at which gas is ordinarily tested.

(*f*) The usual barometer corrections are applied. The correction to standard gravity is usually omitted, being generally less than 1 in 1000. The temperature correction to reduce the observed barometric pressure to the standard pressure, defined in terms of mercury at 32° F, was taken from a table.

(*g*) An aspiration psychrometer of the Assmann type was used, and the humidity corresponding to the observed readings of the wet and dry bulbs was taken from a table.

(*h*) The meter was calibrated immediately after the experiment by the aspirator-bottle method, fully explained on page 35. This gave the volume delivered for two turns of the meter at the temperature of the meter (85.6°) and at the pressure on the gas in the meter (29.75 inches). The factor for reduction to standard conditions of temperature (60° F) and pressure (30 inches) was taken from a table.

(*i*) This correction for loss of heat to surroundings may usually be neglected. Its magnitude depends on the design of the calorimeter, the rate of gas consumption, and the rise in temperature of the water. This correction is considered on page 52.

(*j*) This correction is generally neglected. It is discussed on page 10.

(*k*) This is the total heating value, as defined on page 13, of the sample of gas tested.

(*l*) This is the net heating value, as defined on page 14, of the sample of gas tested.

The standard temperature and pressure to which measured volumes of gas (saturated with water vapor) are referred, in the United States and in Great Britain, are 60° F and 30 inches of mercury (at 32° F). The correction factors by which the volumes of gas, saturated with water vapor, observed at various temperatures and pressures must be multiplied to reduce to these standard conditions of pressure, temperature, and saturation, may be taken from tables prepared for this purpose.

2. CONSTRUCTION AND MODE OF OPERATION OF METERS

The amount of gas burned in calorimetric and photometric tests is generally measured by small gas meters of the wet-meter type. In some calorimeters (e. g., the Doherty and the Parr calorimeters) the volume of the gas burned is defined by displacing a definite volume of the gas by means of water and forcing the gas thus displaced to flow through the burner in the calorimeter.

The cases of such meters are made of cast iron, steel, or brass, protected by a coating of tin, nickel, japan, or enamel, and sometimes of porcelain.

The dials of these meters are generally graduated so that one complete revolution of the drum, and therefore of the index moving over the dial, corresponds either to one-tenth or one-twelfth cubic foot or to 3 liters. One-twentieth cubic foot meters are also made for inspection work.

Some meters are provided with a second graduated dial on which the rate in cubic feet per hour can be read by one minute's observation. If, however, only a fraction of a turn is read, the results may be considerably in error. (See p. 33.) For this reason photometric meters are usually made to deliver one-twelfth cubic foot per revolution, so that the rate of 5 cubic feet per hour corresponds to one whole revolution of the index in one minute.

The measuring drum of the meter and the shaft and bearings are usually made of some metal or alloy (e. g., tinned brass, Britannia metal, German silver, special bronzes, etc.) which will resist the action of sulphur compounds, ammonia, etc., that may be present in the gas. The stuffing box of the front bearing of the drum is usually accessible by removing the face dial, so that the bearing can be repacked when necessary. In some meters the other bearing is completely surrounded by water.





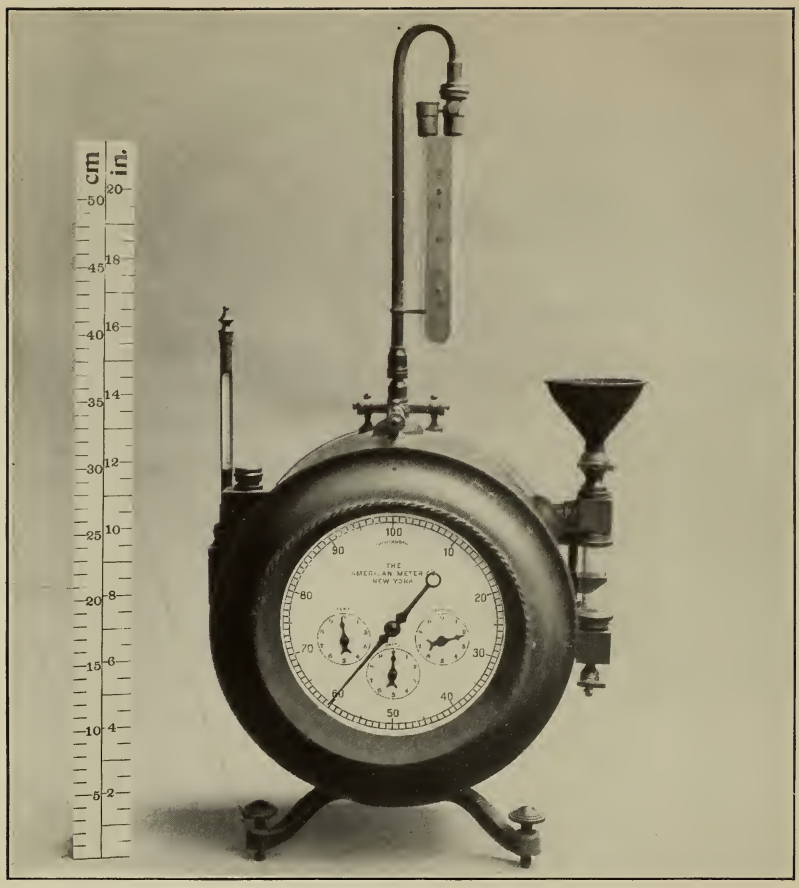




Fig. 3.—*Laboratory gas meters*

To reduce the error in adjusting the water level this adjustment should be made when the drum is in a definite position, e. g., when the index is at zero. The index should therefore be so securely fastened to the shaft of the drum that it can not easily be displaced relatively to it. There are four points in each revolution of the drum when there are considerable fluctuations of the water level and the index should be so mounted on the shaft as to pass through zero about halfway between two such fluctuations.

Descriptions of special features of construction of gas meters may be found in trade catalogues. Two of the meters used in this investigation are illustrated in Fig. 3.

The volume of gas delivered per revolution depends upon the volumes of the compartments of the drum and upon the position of the surface of the water. Hence, it is important that the water level be accurately reproducible. This is secured by mounting the meter on leveling screws, providing it with a suitable level indicator and with a suitable water gauge.

The usual level indicators are (*a*) two spirit levels at right angles, (*b*) circular spirit level, (*c*) plumb bob. The first named is certainly the most convenient to use and probably can be made the most accurate. The sensibility of the levels should correspond with that of the leveling screws; that is, a small motion of the screw should produce a visible motion of the bubble of the level.

The water-level devices commonly used are (*a*) an automatic overflow; (*b*) sight box, which is simply an extension of the meter casing; (*c*) a gauge glass. The glass front of the sight box has a reference mark to which the water level is adjusted. The gauge glass has either a reference mark etched on it or some form of pointer. The latter has the advantage (or disadvantage) of being adjustable. A device used on one meter tested, consisting of two knife edges located one on each side of the gauge glass, proved very satisfactory. Experiments showed that there was little choice between the sight box and the gauge glass as far as reproducibility of water level was concerned, but the automatic overflow was decidedly inferior to either.

Briefly, the mode of action of wet meters is as follows:

The cylindrical measuring drum, rotating on a horizontal axis, is divided into four specially-shaped measuring compartments by

suitable partition walls, with nearly radial outlets on the front face and similar inlets on the back face of the drum. (See Fig. 4.) The drum is immersed in water to a depth of nearly two-thirds its diameter. Gas is admitted into the inlet chamber, which forms a fifth compartment at the rear of the drum, as shown in Fig. 5.

The measuring compartments are so shaped that the two nearly radial openings of a compartment in the back and front face of the drum, respectively, are at an angle of about 160°. The water level must be sufficiently high to seal off the opening in the inlet chamber through which the inlet tube and the shaft of the drum pass and to momentarily seal off both openings of the measuring compartment at the highest point of its revolution. The nearly radial openings in the front face of the drum are shown in Fig. 4. The shaded areas in this figure show the shape of one compartment. The mode of operation may be understood by following one compartment through a complete revolution. Starting with the compartment at its lowest point, both openings are under water and the compartment is filled with water. As the drum revolves, the opening at the rear passes out of the water and the gas enters, the water running out at the front opening. As the drum continues to turn, the compartment continues to fill with gas until it comes nearly to the top position. However, before the opening at the front emerges from the water the one at the back is closed by the water, thereby sealing off momentarily a certain volume of gas. As the drum continues to revolve the opening at the front emerges from the water and the gas escapes, being displaced by water entering at the back opening, until the compartment is again entirely submerged. It will be seen from the above description that in the operation of the meter both the gas and the water are caused to pass through the drum from back to front. Each compartment during each revolution delivers the amount of gas it contains at the instant it is sealed off. This amount will evidently depend upon the water level. The motive power is furnished by the difference of pressure of the gas on the two sides of the inclined partitions in the drum.

3. PREPARATION OF THE METER FOR USE

After filling the meter with water approximately to the gage mark, the meter was run for some time until the water was satu-



Fig. 4.—*Measuring drum of laboratory gas meter, showing radial openings of compartments. The blackened areas indicate the shape of one of the four measuring compartments*

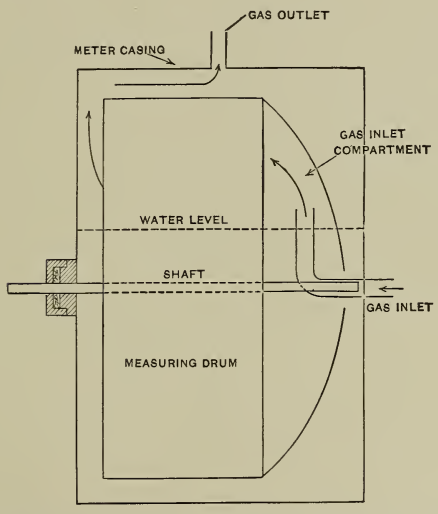


Fig. 5.—*Section illustrating mode of operation of laboratory gas meter*

rated with the gas to be used. This preparation is more important in photometric than in calorimetric measurements. (See p. 95.)

The meter was then leveled and the water level adjusted to the gage mark. This adjustment was made as follows: With the index at zero and both inlet and outlet open to the air and a small excess of water in the meter, water was withdrawn until the water level was brought to the gage mark. The meter was then run one more revolution and the adjustment verified. Different methods of making this water-level adjustment will give quite different calibrations, e. g., adjusting the water level with the meter running may make a difference greater than 1 per cent with some meters. The water-level adjustment should therefore be made in the same way when the meter is calibrated and in its subsequent use. The above method is recommended as giving reproducible results. With due care the accuracy of adjustment of the water level is within 0.01 inch; that is, about 0.2 per cent in the calibration constant of these meters. If the gas is drawn from the mains, it may not be completely saturated, in which case it will take up water vapor and slowly lower the level of the water in the meter.

4. METHOD OF USE

These meters may be used in either of two ways: (*a*) The meter is calibrated in absolute measure each time it is used, or at least very frequently, e. g., by means of a cubic foot or other standard bottle, and (*b*) the meter is calibrated once for all and depended upon to retain this calibration when properly adjusted.

It was concluded from a large number of tests that a laboratory meter after being calibrated could be subsequently used for short periods (one or two days) to an accuracy of 0.2 per cent, so long as the level of the meter was not disturbed and the water level was not changed, either by readjusting or as the result of leakage or evaporation. How long a time these conditions would hold would obviously depend on such factors as the presence of leaks in the stuffing boxes, the degree of saturation of the gas passed through the meter, etc. The above conclusion is probably not applicable to the Elster or other internal overflow meters. If the meter is to be calibrated once for all, and then used as a secondary standard, the question of the reproducibility of the water level, etc., becomes an important one.

5. INVESTIGATION OF SOURCES OF ERROR

Experiments were made to determine the effects of errors in making the adjustments with such meters.

(a) **Method Used.**—For this purpose two meters were used in series. This method of comparing one meter with another can be used to determine to within 0.1 per cent the ratio of the volumes of gas delivered by the two meters, provided that care is taken to secure equality in the temperatures of the meters and of the room. The fact that one meter left undisturbed could be taken as constant to this degree of accuracy was established both by absolute calibrations and by determining the ratio to other meters also undisturbed.

The observations taken in comparing two meters in series are shown in Table 4. One observer gave a signal as the index of one meter passed the graduations noted in columns 1, 3, and 5, while the second observer noted the simultaneous readings of the second meter as recorded in columns 2, 4, and 6.

TABLE 4

Comparison of Meters No. 6312 and No. 246

[Temperature of meter No. 6312=80°0 F; temperature of meter No. 246=79°8; room temperature=80°6; rate=4.3 cubic feet per hour]

	First series		Second series		Third series	
	Meter No. 6312	Meter No. 246	Meter No. 6312	Meter No. 246	Meter No. 6312	Meter No. 246
	Cubic feet	Cubic feet	Cubic feet	Cubic feet	Cubic feet	Cubic feet
Initial readings	36.3800	11.4194	36.4800	11.5202	36.5800	11.6205
	.3900	290	.4900	293	.5900	300
	.4000	392	.5000	395	.6000	402
	.4100	483	.5100	486	.6100	494
	.4200	594	.5200	597	.6200	605
	36.4000	11.4391	36.5000	11.5395	36.6000	11.6401
Final readings	36.8800	11.9221	36.9800	12.0226	37.0800	12.1230
	.8900	318	.9900	322	.0900	327
	.9000	416	37.0000	420	.1000	424
	.9100	507	.0100	514	.1100	515
	.9200	618	.0200	623	.1200	628
	36.9000	11.9416	37.0000	12.0421	37.1000	12.1425
	36.4000	11.4391	36.5000	11.5395	36.6000	11.6401
Difference	.5000	.5025	.5000	.5026	.5000	.5024

Correction to No. 246 for difference in temperature=+0.0003, therefore 5.028 turns of No. 246=5.000 turns of No. 6312.

(b) **Leveling.**—If the meter is set up and the water level adjusted, then, tilting the meter in various directions up to 1° of arc (about 2 turns of leveling screw, 18 threads per inch) without changing the amount of water in the meter, produced no change exceeding 0.2 per cent in the calibration. However, readjusting the water level when the meter was tilted so that the gauge mark was raised or lowered through an angle of 1° with the horizontal caused a change in calibration of about 1.6 per cent.

(c) **Adjustment of Water Level.**—Investigation of several 0.1 cubic foot meters of different makes showed that a change in water level of 1 mm (0.04 inch) produced a change in calibration of from 0.5 to 0.8 per cent in the different meters, the meters delivering a smaller volume of gas per revolution when the water level was higher. It follows, therefore, that in order to reproduce the calibration to an accuracy of 0.1 per cent, the total error in adjusting the water content of the meter, whether the error be due to error in leveling or in adjusting water level, must not exceed the equivalent of 0.1 or 0.2 mm in the position of the water level in the gauge glass.

(d) **Temperature, Humidity, and Pressure.**—The actual quantity (i. e., mass) of gas delivered by the meter per revolution depends not only upon the volume of the compartments of the measuring drum and the position of the surface of the water, but also upon the temperature, humidity, and pressure of the gas in the measuring compartments. The meter must therefore be provided with a thermometer, so placed in the meter (preferably with the bulb in the water) as to indicate, as nearly as possible, the temperature of the gas in these compartments. While the temperature of the gas in the rotating drum can not be directly measured, this temperature will be approximately that of the water in the meter, provided that the temperature of the gas as it enters the meter does not differ too much from the temperature of the meter and that the meter is approximately at room temperature. As the water in the meter is well mixed by the movement of the drum, the temperature will be very nearly uniform throughout. An error of 1° F in the temperature of the gas will cause an error of approximately 0.3 per cent in the measurement of the gas.

Gas taken from a small holder with water seal is delivered to the meter practically saturated. To determine the effect of delivering relatively dry gas to the meter, the following experiment was made: Gas from the holder was passed through a copper coil immersed in ice to remove the moisture and then through two meters in series. In passing through the iced coil the saturation temperature of the gas was reduced to about 37° F. It was found that the calibration of the first meter, supplied with dried gas, did not change more than 0.1 per cent relative to the second meter from the calibration obtained when the first meter was supplied with saturated gas. The temperature of the meters was 75° F and the rate 7 cubic feet per hour. Humidity tests of the gas delivered by the first meter, when supplied with dried gas, showed the gas delivered to be saturated at the meter temperature. These experiments show that, at this rate, the gas was actually metered at the temperature indicated by the thermometer in the meter and that it had become practically saturated at that temperature.

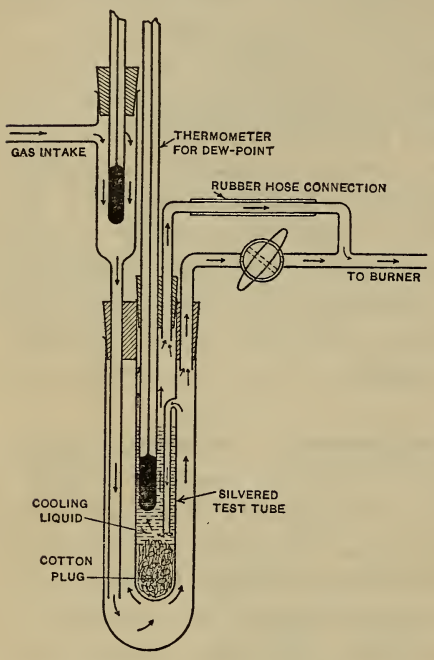


Fig. 6.—*Dew-point hygrometer*

The humidity of the gas was measured with a dew-point hygrometer, diagramatically shown in section in Fig. 6. The lowering of temperature of the inner silvered test tube was produced by evaporation of a volatile liquid and could be conveniently controlled by regulating the amount of gas passed through the stopcock. The dew point was directly read from the thermometer, the bulb of which was immersed in the liquid (ether or alcohol, depending on the lowering of temperature required) contained in the silvered test tube. The cotton plug in the bottom of the silvered test tube

prevented the cooling of this portion and the presence of dew was thus readily distinguishable by contrast between the bright surface below and the immediately adjacent surface above covered with a deposit of dew.

The effective pressure of the gas, when measured in the compartments of the meter drum, is the pressure in the inlet chamber and is practically equal to the pressure at the inlet of the meter. This pressure is usually a few inches of water above atmospheric pressure, corresponding to a few tenths of an inch of mercury, which must be added to the atmospheric pressure to find the pressure under which the gas was measured. If the inlet pressure is 2 inches of water, the corresponding correction due to this cause is about 0.5 per cent of the total pressure.

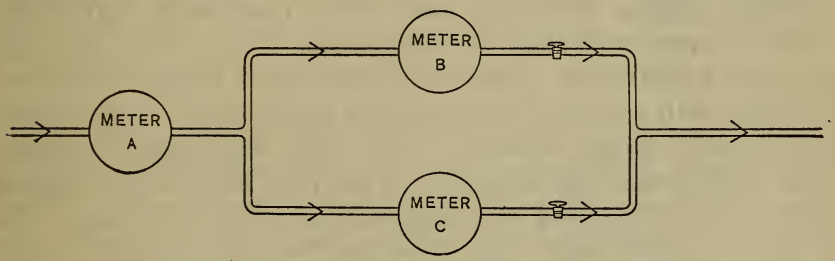


Fig. 7.—*Series-parallel arrangement of gas meters*

(e) **Variation of Calibration with Rate.**—The effect on the calibration of running these meters at different rates was tested in two ways—(*a*) by calibrations at different rates with a standard meter prover, and (*b*) by connecting three meters in a series-parallel combination, as shown in Fig. 7. The meter A, under test, was calibrated at a given rate, e. g., 5 cubic feet per hour, against B and against C, successively. Then A was calibrated at 10 cubic feet per hour against B and C running in parallel, each at 5 cubic feet per hour. B and C running at 10 cubic feet per hour were also tested against A at 10 cubic feet per hour. Since the effect of the given change of rate on A was known from the previous experiment, the effect of the change of rate on B and C was at once deducible. The conclusion from a series of such experiments was that the volume of gas delivered per revolution by these meters (one-tenth cubic foot), at rates between 2 and

10 cubic feet per hour, was constant to within about 0.1 per cent. This conclusion was further supported by the results of measurements of the drop in pressure through such meters. These measurements showed that the total drop was less than 0.1 inch of water and that the increase in the pressure drop, at rates between 2 cubic feet and 10 cubic feet per hour, was less than 0.01 inch of water; the consequent change in the water level must have been still smaller. Experiments with the meter prover showed that the meters delivered more gas per revolution at the higher rates—about 0.5 per cent more at 20 cubic feet and about 1 per cent more at 30 cubic feet per hour.

(f) **Reproducibility of the Calibration.**—To determine the reproducibility of the calibration the meter under investigation was emptied, refilled, releveled, water level readjusted, and recalibrated a number of times by comparison with a meter that had been left undisturbed. Such experiments on a number of meters, provided with sight box or gauge glass for water level adjustment, showed an average deviation of 0.1 per cent from the mean, with a maximum difference of 0.4 per cent between the highest and lowest calibrations for a series of six or more refillings. The order of reproducibility may therefore be put at about 0.2 per cent, although the error may evidently attain nearly 0.5 per cent. With an Elster internal-overflow meter differences in calibration, for different fillings with water, as great as 1 per cent were obtained. As the water level is not visible in this type of meter, the water level may vary considerably without the knowledge of the observer.

As an illustration of the behavior of a meter under working conditions there are given in Table 5 all the results of absolute calibrations of meter No. 6312, illustrated in Fig. 3, and which were made during a period of nearly two years. The meter was provided with a small plumb bob for leveling and the water level was adjusted to a mark on the glass of the sight box. Each calibration corresponds to a single adjustment of water level and is the mean of several calibrations by the aspirator bottle method. (See p. 35.) The variations among the calibrations made on different days but corresponding to a single adjustment of water level are nearly as great as among the tabulated mean values

corresponding to different adjustments of the water level, indicating that the variations are to some extent to be attributed to errors in the absolute calibrations.

TABLE 5

Absolute Calibrations of Meter, B. S. No. 6312

Date of calibration	Volume delivered per turn	Calibrated with—
	Cubic feet.	
November 6, 1911	0.1007	Illuminating gas.
October 5, 1912	.1003	Do.
October 8, 1912	.1004	Do.
June 17 to June 24, 1913	.1005	Natural gas.
July 21 to August 7, 1913	.1007	Illuminating gas.
August 12, 1913	.1009	Hydrogen.
Mean	.1006	

Experiments were also made on the method of adjusting the water level by filling the meter with water to a constant total weight. For this purpose two meters were connected in series, one meter being mounted on the pan of a balance. Intercomparisons of the two meters were made by the method illustrated by Table 4. From a series of eight experiments it was found that the calibration of the weighed meter, which was emptied and refilled before each intercomparison, could be reproduced to within 0.1 per cent, the maximum difference between any calibrations being less than 0.2 per cent. This method of adjusting the water level may sometimes be of use in permanent laboratory installations. If this method is used, the outer casing of the meter should be sufficiently rigid to withstand deformation. (For large variations in temperature a correction would also be necessary (of the order of 1 part in 10 000 per 1° F) for change in water level due to change in temperature.) The principal value of these experiments, however, consists in showing that reproducible calibrations may be attained if the water level adjustment is correctly made.

(g) **Fractional Revolutions.**—In the instructions for use accompanying some meters the use of fractional revolutions is specified.

This procedure is not to be recommended, as it may lead to very significant errors. For example, a test of one of these meters, the motion of the index of which over the scale was very regular, gave the results shown in Table 6.

TABLE 6 [8]

Volumes of Gas Delivered in Fractional Revolutions of Meter

Fractional revolution	Volumes of gas delivered	Volume delivered divided by 2820
	cc	
0.250	732	0.260
.333	972	.345
.500	1474	.523
.667	1924	.682
.750	2156	.765
1.000	2820	1.000

[8] The method of calibration used in the experiments summarized in this table was the aspirator bottle method, described on p. 35.

It will be seen that the volume of gas delivered in the second half revolution was 8.7 per cent less than in the first half revolution, and the volume delivered in the last one-third revolution was 7.8 per cent less than in the first one-third revolution. The quarter revolutions show similar differences. These meters should therefore be calibrated and used for total revolutions, or, if fractional revolutions must be used, the particular portion of the scale used must be calibrated.

(h) **Effect of Resistance to Rotation.**—All the conclusions stated above as to the accuracy of these meters, reproducibility of calibration, and independence of rate are true only if the meter is not required to do an appreciable amount of work, either in overcoming friction in the bearings or in overcoming resistance in a recording or other mechanism. If the meter is required to do work, there will be a difference of water level on the inlet and outlet sides, on account of the difference in pressure necessary to overcome the resistance, and the capacity of the drum will be changed by the change in level due to this cause to the same extent as by an error in adjusting the water level. The importance, therefore, of having the drum rotate so easily that the drop in pressure through the meter remains sensibly constant is readily seen. A criterion

as to the proper working of the meter may be obtained by determining whether the calibration is independent of the rate (up to about 10 cubic feet per hour). Such a determination may readily be made by using the aspirator bottle method of calibration.

6. ABSOLUTE CALIBRATION

These meters may be calibrated (*a*) by comparison with a standard meter prover, (*b*) by measurement of the volume of water displaced from a suitable container by the gas passed through the meter, and (*c*) with a standard bottle of known capacity.

(a) **Meter Prover.**—The meter prover must itself be tested against some standard volume, such as a cubic-foot bottle. The accuracy then attainable with it is less than the accuracy attainable with the wet meter, because of the difficulty of determining the temperature of the gas in the prover. Calibration with the meter prover is more time consuming than the other methods of testing small wet meters, as several cubic feet of gas must be run through the meter to obtain a sufficient length of scale reading on the prover to permit reading the scale length with the required accuracy. The meter prover is generally used for testing service meters, and is not well adapted to the testing of laboratory meters.

(b) **Aspirator Bottle.**—A simple, accurate, and inexpensive equipment for calibrating laboratory meters by the displacement method, using an aspirator bottle, is shown in Fig. 8. The volume of gas drawn through the meter for a given number of revolutions of the index is calculated from the corresponding weight of water displaced from the bottle. Before measurements are made, the water in the bottle should be saturated with the gas by displacing the water with the gas and refilling the bottle with the same water, repeating the operation several times.

If the highest accuracy is sought and the corrections are to be reduced to a minimum, it is necessary that the temperature of the gas entering the meter, of the water in the meter and in the bottle, and of the room be the same. These conditions are usually not difficult of attainment, within the requisite limits, if the temperature of the room is fairly constant. The main advantages of this method are (*a*) the temperature of the gas in the bottle is determinable since the gas passes through a tube in the large mass

of water, the temperature of which is that of the bottle and given by a thermometer suspended therein, and (*b*) the meter can be calibrated for the conditions of use with the calorimeter, viz, for the amount of gas delivered between successive passages of the index of the meter through the zero position.

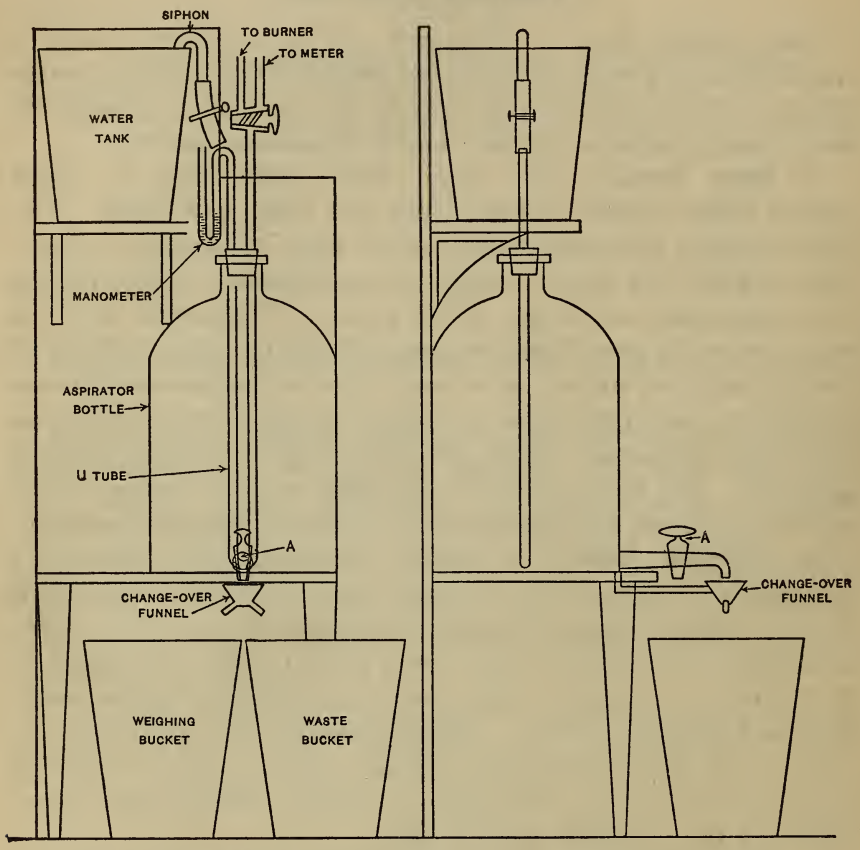


Fig. 8.—*Arrangement for calibrating gas meters by the aspirator bottle method*

The observations are made as follows: The apparatus is allowed to stand with the gas pressure on and with the lower stopcock, A, closed until it is evident that there are neither leaks nor absorption of gas by the water. With the change-over funnel set to allow the water to run to the waste bucket, the stopcock, A, is opened. As the index of the meter passes through the zero position the change-over funnel is shifted to allow the water to run into the

weighing bucket. After the index of the meter has made the desired number of revolutions, the funnel is shifted back just as the index passes through the zero position. The stopcock, A, is then closed. The volume of gas delivered is calculated from the weight of the water displaced. A sample observation showing the method of reduction is given in Table 7.

To refill the bottle with water the siphon tube is connected to the manometer, the three-way stopcock turned so as to permit the gas in the bottle to escape through a burner, the siphon started, and the gas lighted at the burner.

It is evidently possible by manipulating the stopcock, A, to use the method in the same way that the standard bottles (one-tenth cubic foot, etc.) are used, viz, by starting with the meter at rest and stopping it, after the desired number of revolutions, with the index in the initial position. The amount of gas delivered for any given fraction of a revolution may also be found.

TABLE 7

Calibration of Meter by Aspirator Bottle Method

Time	Start	2 : 54 : 38	End	2 : 59 : 17	
Meter reading, cubic feet		46. 6000		46. 9000	
Room temperature, degrees centigrade					25. 4
Meter temperature, degrees centigrade					25. 8
Bottle temperature, degrees centigrade					25. 2
Gas pressure at meter inlet, millimeters of water					36
Gas pressure in bottle, millimeters of water					28
Weight of water, grams					8481
Computation:					
Weight of water, grams					8481
Correction for buoyancy					+ 9
Correction for density of water					+25
Correction of difference of temperature of gas in meter and in bottle					+27
Correction for difference of pressure of gas in meter and in bottle					− 7
Volume of gas passed into meter, cubic centimeters					8535

1 revolution of index $=\frac{8535}{3}=2845$ cubic centimeters=0.1005 cubic feet.

A résumé of a large number of calibrations of different meters by this method has shown that the accuracy of a single determination is of the order of 0.2 per cent. The meters were found to measure the same volume of gas per revolution when tested as

ordinarily used with a calorimeter (i. e., for successive passages of the index of the meter through zero), or when tested with the index started from rest at zero and brought to rest at zero. The conclusion was that calibration by the latter method, which is that of the standardized bottle, introduced no error exceeding 0.1 per cent when the meter was used as it is with the calorimeter.

(c) **Standardized Bottles.**—Cubic foot or other standard volume bottles of suitable design may be used with considerable accuracy if the proper precautions are observed. For calibrating the gas meters used in calorimetry and photometry, small one-tenth or one-twelfth cubic foot bottles, of the type illustrated in Fig. 9, are often used. As the volume of the bottle may be determined from the mass of water necessary to fill it and the density of the water at the observed temperature, the error in this determination should be negligible. The change in the volume of the bottle itself due to change in temperature may in general be neglected. The temperature of the water in the standard bottle and in the meter under test should be as nearly as possible equal to the room temperature.

With the immersion type of bottle considerable error may be introduced due to the cooling of the bottle and the contained gas by evaporation from the outer wet surface of the bottle. As ordinarily used there may be a large error in the temperature assigned to the gas contained in bottles of this type, unless the air in the room is saturated.

The gas connections should always be tested for leaks before beginning the meter calibrations. If the meter and bottle are used with gas, the water with which the bottle is filled should preferably be saturated with the gas. If the bottle is filled with gas from a small holder with water seal, the gas will be practically saturated; if only partially saturated gas is used, it will become saturated in a short time if the inner walls of the bottle are wet.

In the ordinary method of use of standardized bottles a volume of gas, determined by the positions of upper and lower graduation marks on the bottle, is displaced through the gas meter. At the beginning and end of the displacement of gas from the bottle the pressure on the gas is only slightly in excess of atmospheric pres-

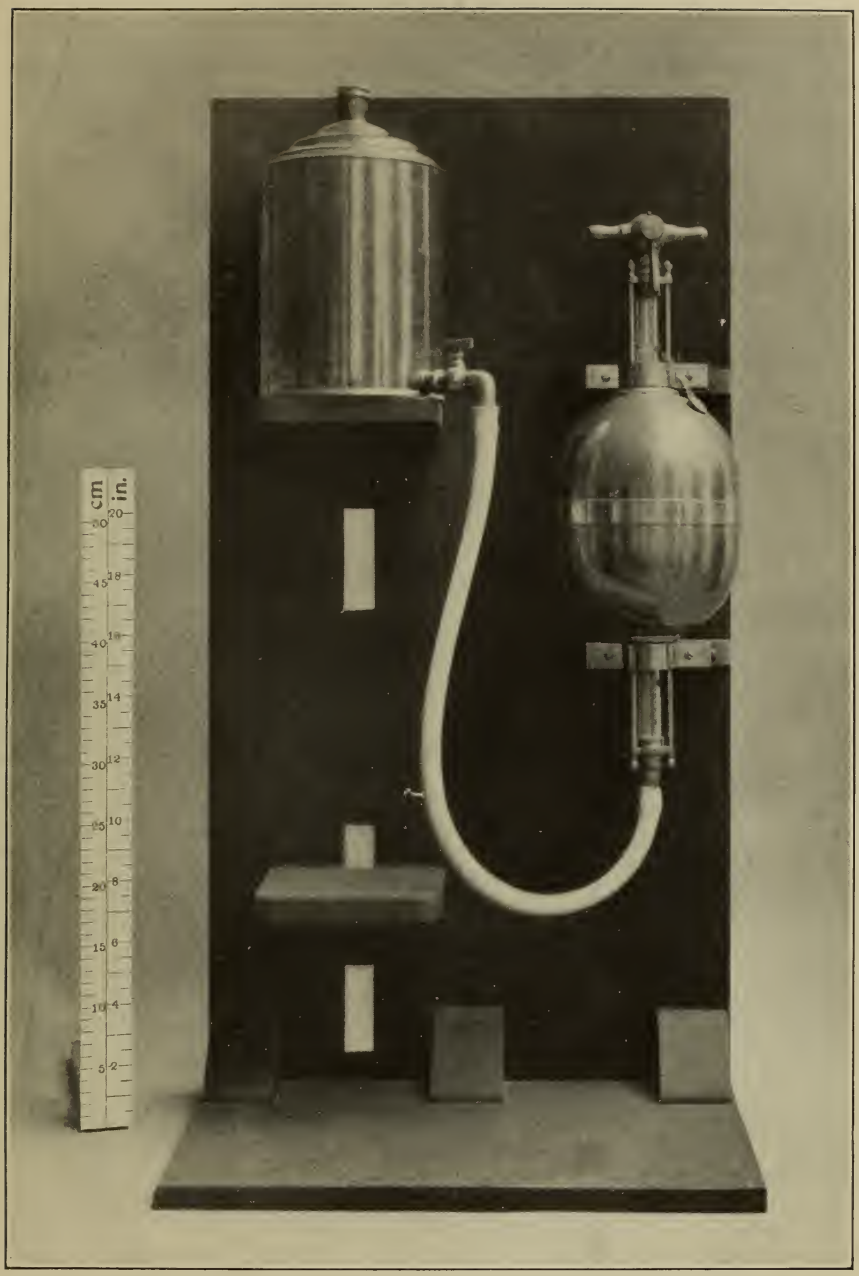


Fig. 9.—*Standard volume bottle used for calibrating gas meters. Volume = 0.1 cubic foot*

sure, due to the static back pressure of the meter. The gas in the bottle is therefore measured practically at atmospheric pressure. When the meter is running the gas is under a somewhat higher pressure and is measured by the meter at this pressure; that is, its volume is smaller when measured in the meter. For a meter in good running order this excess of pressure, at the rates ordinarily used, is small enough to be neglected, being less than one-tenth of an inch of water.

A comparison of the aspirator bottle method of calibration, described on page 35, with the standardized bottle method was obtained by calibrating the same meter, first by the displacement method and then with a one-tenth cubic foot bottle. The standard bottle was used in two ways, first as above described and then by displacing the water in the bottle by gas which had been passed through the meter. The latter method has two advantages—(*a*) the temperature of the gas in the bottle may be more accurately determined since it is very nearly that of the water which has just been displaced, (*b*) there is less probability that the gas will be absorbed by the water in the bottle when the water is flowing out of the bottle than when it enters in a jet. Results obtained by the three methods are shown in Table 8.

TABLE 8

Comparison of Standard Bottle and Aspirator Bottle Methods of Calibration of Meters

(*a*) By aspirator-bottle method, one-tenth cubic foot=0.996_6 turn of meter.
(*b*) By one-tenth cubic foot bottle, displacing gas from bottle through meter, one-tenth cubic foot=0.996_0 turn of meter.
(*c*) By one-tenth cubic foot bottle, displacing water from bottle by gas from the meter, one-tenth cubic foot=0.997_3 turn of meter.

The results show that the methods are in satisfactory agreement.

7. SUMMARY OF METER TESTS

The meters used in these tests were: American Meter Co., one-tenth cubic foot; Elster, 3 liter; Sargent, one-tenth cubic foot; Alexander Wright & Co. (Ltd.), one-tenth cubic foot; John J. Griffin & Sons (Ltd.), one-twelfth cubic foot.

A large number of tests have shown that these meters, with the exception of the Elster with internal overflow, can be used to an accuracy of about 0.2 per cent when calibrated against a standard volume before use and, with due care in adjustment, may be used by different observers to reproduce an absolute calibration from time to time to within 0.5 per cent, provided the meter has suffered no mechanical injury, such as displacement of levels or of gage mark.

The calibration of the meters was found to be independent of the rate (to within 0.1 per cent) for rates of 2 to 10 cubic feet per hour. At 20 cubic feet per hour the meters were slightly slow (about 0.5 per cent).

The use of fractional turns may lead to significant errors, e. g., in the determination of the rate of flow in photometric tests. In one of the most smooth running meters examined the amount of gas delivered in the last one-third revolution was about 8 per cent less than in the first one-third revolution, with similar differences for other fractional turns. If fractional turns are used, the dial should be calibrated, e. g., by the aspirator bottle method.

It was found that the method of calibration by the standardized bottle, in which the meter is started from rest and again brought to rest, after a given volume of gas has passed through it, gave a calibration in agreement, to within 0.1 per cent, with a calibration made by determining the amount of gas delivered between successive passages of the meter index through the zero position.

The precautions to be observed in setting up the meter, such as leveling, adjusting of water level, saturating water in meter with the gas to be tested, the reduction of measured volumes to standard conditions of temperature, saturation and pressure, methods of absolute calibration of meters, and details of construction of meters have been considered in the preceding sections.

It will subsequently be seen that the accuracy with which the gas can be metered is of the same order as the accuracy with which some of the other factors which enter into a calorimetric measurement can be determined.

VII. FACTORS AFFECTING HEATING VALUE DETERMINATIONS WITH FLOW CALORIMETERS

The various factors which may influence the results of determinations of the heating values of gases by means of flow calorimeters may be somewhat arbitrarily divided into four groups, as follows:

(*a*) Those that affect the temperature measurements and the quantity of heat absorbed by the water, discussed under sections 1 to 7, inclusive.

(*b*) Those that affect the measurement of the amount of water run through the calorimeter during a test, discussed under sections 8 and 9.

(*c*) Those that affect the measurement of the volume of gas burned during a test, discussed under sections 10 to 12, inclusive.

(*d*) Certain factors depending upon the properties of the gas (particularly some illuminating gases) tested, discussed under sections 13 to 16, inclusive.

1. COMPLETENESS OF COMBUSTION

The question as to whether the combusion of the gas in the Bunsen burner of the calorimeter is complete could probably be most directly answered by a chemical analysis of the gas and of the products of combustion. While no such analyses have been attempted, considerable evidence has been obtained, all of which goes to show that the combustion of illuminating gas, natural gas, and hydrogen, in suitable burners, is complete within at least 0.2 or 0.3 per cent. Thus, in the experiments with natural gas burned in the Junkers calorimeter (see p. 104), different burners were used, the character of the flame was varied, etc., yet the heating values found for a given sample of gas were practically the same under all the different conditions. The experimental data summarized in Table 9 may be cited as typical of a large number of observations obtained during the progress of this investigation.

TABLE 9

Effect of Varying Character of Bunsen Flame

Character of Bunsen flame						Remarks
Normal		Partly luminous		Large excess of air; roaring		
Total	Net	Total	Net	Total	Net	
Btu	Btu	Btu	Btu	Btu	Btu	
685	622	.....	.....	685	622	Junkers calorimeter; illuminating gas.
753	682	753	679	751	678	Do.
683	628	683	629	684	629	Do.
.....	.....	638	.....	637	.....	Boys calorimeter; illuminating gas. Glass tube Bunsen burner.
999	902	.....	.....	998	901	Junkers calorimeter; natural gas.
.....	.....	.....	.....	996	901	Same, with Méker burner.

In Table 10 are summarized experiments made with the Boys calorimeter provided with a luminous flame burner which also indicate that, under ordinary conditions, the combustion is quite complete.

TABLE 10

Effect of Incomplete Combustion on Heating Value

Observed heating value, Btu	Gas rate, cubic feet per hour	Remarks
654	4.0	No evidence of incomplete combustion.
647	4.73	Dense smoke issued from calorimeter.
632	4.83	Very dense smoke.

It will be seen that the observed heating value had only been lowered by 1 per cent when dense smoke was issuing from the calorimeter. In several instances distinctly visible discharge of smoke from the calorimeter was noticed without any perceptible effect on the heating values found. With the Bunsen flame there is, however, a very evident drop in heating value as soon as incomplete combustion can be detected by the odor of the outlet products.

The effect of allowing the flame of the Bunsen burner to play against the inner wall of the combustion chamber of the Junkers calorimeter was tried and was found to cause no change in the

observed heating value. It did, however, result in increasing the irregularities in the readings of the outlet-water thermometer of the calorimeter.

That the combustion in the Bunsen burner must be very nearly complete would also seem to be indicated by the results of determinations of the heating value of a gas with very different ratios of volumes of air to gas (the so-called capacity-efficiency curves), such as are illustrated in Fig. 14, in which experiments the value of the ratio was varied from 20/1 to 7/1, and yet, under these very different conditions of air supply, the heating values found were the same.

Further corroborative evidence that the combustion is complete is furnished by the excellent agreement of the heating values found for natural gas and for hydrogen using the flow calorimeters, with the values found in calorimeters of the Berthelot bomb type, in which most perfect conditions for complete combustion are realized.

2. TEMPERATURE MEASUREMENTS

The inlet and outlet water thermometers should be graduated to 0°.1 C or to 0°.1 or 0°.2 F. For convenience in reading and to avoid errors of parallax, these thermometers should be provided with suitable reading glasses conveniently movable along the stem of the thermometer. If the thermometers are of the stem type and are read with the unaided eye, errors of parallax may be avoided by adjusting the line of sight so that the graduations near the mercury meniscus are seen superimposed on their images reflected from the mercury thread. If the thermometers are of the inclosed scale type, the line of sight should be so adjusted that the portion of the graduation, near the mercury meniscus, seen through the fine capillary stem, is in the same straight line with the ends of the graduation seen on either side of the capillary stem.

The thermometers should be so placed that they assume the true mean temperature of the water entering and leaving the calorimeter; that is, their bulbs must be in the flowing stream of water in such a position that the formation of a dead space around the bulb is not possible. The tops of the bulbs should be sufficiently far (0.5 inch) below the lower surface of the stoppers in which the thermometers are mounted so that the effect of heat

conduction to the bulbs is negligible. On account of the small bulb space available in the inlet and outlet tubes of most calorimeters this condition can not always be realized unless the bulb is made short.

The bulb of the inlet-water thermometer is subject to a slightly higher external pressure than is the bulb of the outlet-water thermometer. In extreme cases an error of 0°.02 F may be introduced due to this cause. Such error may, however, be eliminated by determining the differential correction (see p. 48) with the thermometers mounted in the calorimeter.

It is important that the heated water be thoroughly mixed before reaching the bulb of the outlet-water thermometer. This is usually accomplished by interposing in the path of the water a series of baffle plates. Other methods are also used, some of which are not so effective as might be desired. Thus, the apparent efficiency of one calorimeter tested was somewhat in excess of 100 per cent, which was traced to the fact that the outlet-water thermometer, in the position in which it was used, indicated a temperature higher than the true mean temperature of the effluent water, due to imperfect mixing in the efflux tube.

Sudden and relatively large variations in the readings of the outlet-water thermometer may be due to the accumulation of air bubbles and the formation of an air pocket in the calorimeter, which cause variations in the flow of water, or to air currents in the neighborhood of the calorimeter, which cause variations in the rate of heat transfer to the water. Variations in the rate of water flow, due to trapping of air in the water spaces, can be minimized if all the air is displaced by water, on starting the calorimeter. For example, in the Junkers and similar calorimeters there is little probability that the air will accumulate in the main part of the calorimeter, where the direction of flow is upward. However, at certain rates of water flow air will be trapped in the vertical pipe from the inlet weir. If this air is removed by closing and opening the inlet valve several times, the flow of water becomes and remains quite regular. In some calorimeters air may accumulate under a horizontal or sloping surface, and with such calorimeters there is always more or less irregularity of water flow, e. g., a Junkers calorimeter, new type, (see p. 118) showed this effect.

In other calorimeters, e. g., the Simmance-Abady, air may accumulate under the stopper supporting the inlet-water thermometer and, unless some device is provided to carry off this air, it is necessary to remove it by loosening the stopper from time to time. Variations due to drafts can be reduced in magnitude by shielding the calorimeter from drafts and by the observer avoiding sudden movements during the short time required for the temperature observations.

A sudden drop in the temperature of the inlet water will result in giving an observed heating value that is too high and a sudden rise a value that is too low. Observations in which the temperature of the inlet water varies by more than a few hundredths (0°.05 F) of a degree during the time of a single determination of the heating value should be rejected, unless the method of observation referred to below is used.

The method used by Immenkötter[9] of reading the inlet-water thermometer earlier than the outlet-water thermometer by the length of time required for the water to pass through the calorimeter largely eliminates errors due to variations in the inlet water temperature, and is therefore to be preferred, especially in the absence of thermostatic control of inlet water temperature.

The method of Immenkötter does not take into account the amount of heat involved in the change of the temperature of the metal parts of the calorimeter which occurs when there is a change in the inlet water temperature, and does not therefore completely eliminate the effects of changes in the inlet water temperature. The error, however, is not important, as may be seen from the following considerations. None of the calorimeters weigh much more than 20 pounds. If all of this weight were due to metal in contact with the circulating water, the water equivalent of the calorimeter would be about 2 pounds. In burning 0.2 cubic foot of a 600 Btu gas in a test, the quantity of heat measured is 120 Btu. If the temperature of the inlet water changed 0°.1 F during the test, the error introduced due to the heat capacity of the calorimeter would be 0.2 Btu in 120 Btu, or about 0.2 per cent. If the method of Immenkötter had not been used, the error would have been dependent upon a number of factors, such as water capacity of calorim-

[9] See footnote 5, p. 16.

eter, rate of flow, heat capacity of metal parts, etc., but the error would probably not in any case have been less than that estimated above.

Stem Correction.—Another possible source of error in the temperature measurements arises from the failure to take into account the emergent stem corrections of the thermometers. When the mercury in the stem of a thermometer is at a lower (or higher) temperature than the mercury in the bulb, the thermometer will read too low (or too high), provided it is graduated to read correctly or that it is tested when totally immersed; that is, when the bulb and stem, at least to the mercury meniscus, are at the same temperature. The correction for emergent stem may be computed from the formula:

$$\text{Stem correction} = K \times n\,(T° - t°).$$

K = factor for relative expansion of mercury in glass; 0.00015 to 0.00016 for centigrade thermometers, 0.000083 to 0.000089 for Fahrenheit thermometers, at ordinary temperatures, depending upon the glass of which the stem is made.

n = number of degrees emergent from the bath.

T = Temperature of the bath.

t = mean temperature of the emergent stem.

If the water enters the calorimeter very nearly at room temperature, the stem correction for the thermometer used to measure the temperature of the entering water will be entirely negligible. If the water leaves the calorimeter 18° F (10° C) above room temperature, the emergent stem of the thermometer used to measure this temperature will be at a lower temperature than the immersed portion, and this thermometer will therefore read too low by an amount depending upon the number of degrees emergent and upon the number of degrees by which the mean temperature of the emergent stem differs from the temperature of the bulb.

As an example, approximating conditions often found in practice, assume that the room temperature is 68° F, the observed temperature of the water as it enters the calorimeter is 68°.00 F, and as it leaves the calorimeter 86°.00 F, and that a length of stem of the outlet-water thermometer corresponding to 54° F is emer-

gent from the calorimeter. Under these conditions the average temperature of the emergent stem will be about 70° F. Then

$$\text{Stem correction} = 0.000085 \times 54 \times (86° - 70°) = 0°.07 \text{ F.}$$

Hence the true temperature of the effluent water is 86°.07 F. The stem correction for the inlet-water thermometer, under the above conditions, is obviously zero. If the temperature of the inlet water differs sufficiently (2° or 3°) from the temperature of the room, the stem correction should be computed for the inlet-water thermometer in the same way as shown above. Neglecting the stem correction in the above example would cause an error of 0°.07 in 18° F, or about 1 part in 250; that is, 0.4 per cent in the resulting heating value. Under extreme conditions, with high room temperatures, the error due to neglecting stem corrections may attain 0.5 per cent. For thermometers made in accordance with the Bureau's specifications the error due to neglecting stem corrections would not exceed 0.4 per cent of the temperature interval and would generally be about 0.2 per cent.

Accuracy.—If the inlet and outlet water thermometers are used without being standardized, errors of 0°.3 or 0°.4 F in the usual working interval of 15° to 20° F are possible, which correspond to a quantity of the order of 2 per cent in the resulting heating value (i. e., 12 Btu in 600 Btu). With a careful standardization of the thermometers this possible source of error may be reduced to about 0°.04 F, or 0.2 per cent (i. e., 1 Btu in 600 Btu).

Auxiliary Temperature Measurements.—The effect of errors in the gas meter thermometer is considered on page 29, where it is seen that an error of 1° F in the measurement of the temperature of the gas in the meter causes an error of about 0.3 per cent in the resulting heating value.

An error of 1° F in the measurement of the temperature of the escaping products of combustion will cause an error in the estimation of the sensible heat carried off by the products which is less than 0.1 per cent of the heating value of an ordinary illuminating gas.

The measurement of room temperature does not require a high-grade thermometer so much as it does the proper use of the thermometer to give a true indication of the average temperature of the air in the neighborhood of the calorimeter and gas meter.

The temperature of the room is sometimes read from a thermometer at some distance from the calorimeter, and so placed that its temperature may be influenced by surrounding objects, e. g., steam pipes, flues, windows, walls, etc., under which conditions the indications of the thermometer may give a very erroneous idea of the average temperature of the calorimeter surroundings. In the present investigation room temperatures were measured by the dry-bulb readings of the Assmann psychrometer, placed near the calorimeter. In this instrument the air is circulated past the dry bulb of the thermometer, which is so mounted as to protect the bulb very effectively from the effects of radiation from surrounding objects, and conduction from the metallic parts of the instrument. The position of the psychrometer must of course be judiciously selected so that the air is not drawn over heated or cooled surfaces. An error of 1° F in the estimation of the room temperature would not lead to an error in the resulting heating value exceeding 0.1 per cent, except under unusual conditions.

All of the thermometers used with the calorimeters tested in this investigation were carefully compared with two standard thermometers so that their indications were at once reducible to standard gas-scale temperatures.

Specifications for Calorimetric Thermometers.—Complete specifications in accordance with which calorimetric thermometers have been made up by a number of thermometer makers, and which have proved most satisfactory in every way, will be published in a special Bureau circular. While it is true that, for most purposes, it is desirable to have the ice point on the scale of a thermometer, on account of the convenience with which any secular changes in the thermometer can be measured and allowed for by a determination of the ice point from time to time, this is not necessary for differential measurements, as in calorimetry. If the thermometers have once been standardized, any changes in their corrections relative to one another can easily be determined by intercomparing them at room temperature in a well-stirred pail of water, or while in position in the calorimeter with no gas burning and with the inlet water at room temperature.

If the observed readings of each thermometer are then corrected by the corrections given in the certificates, the difference in these

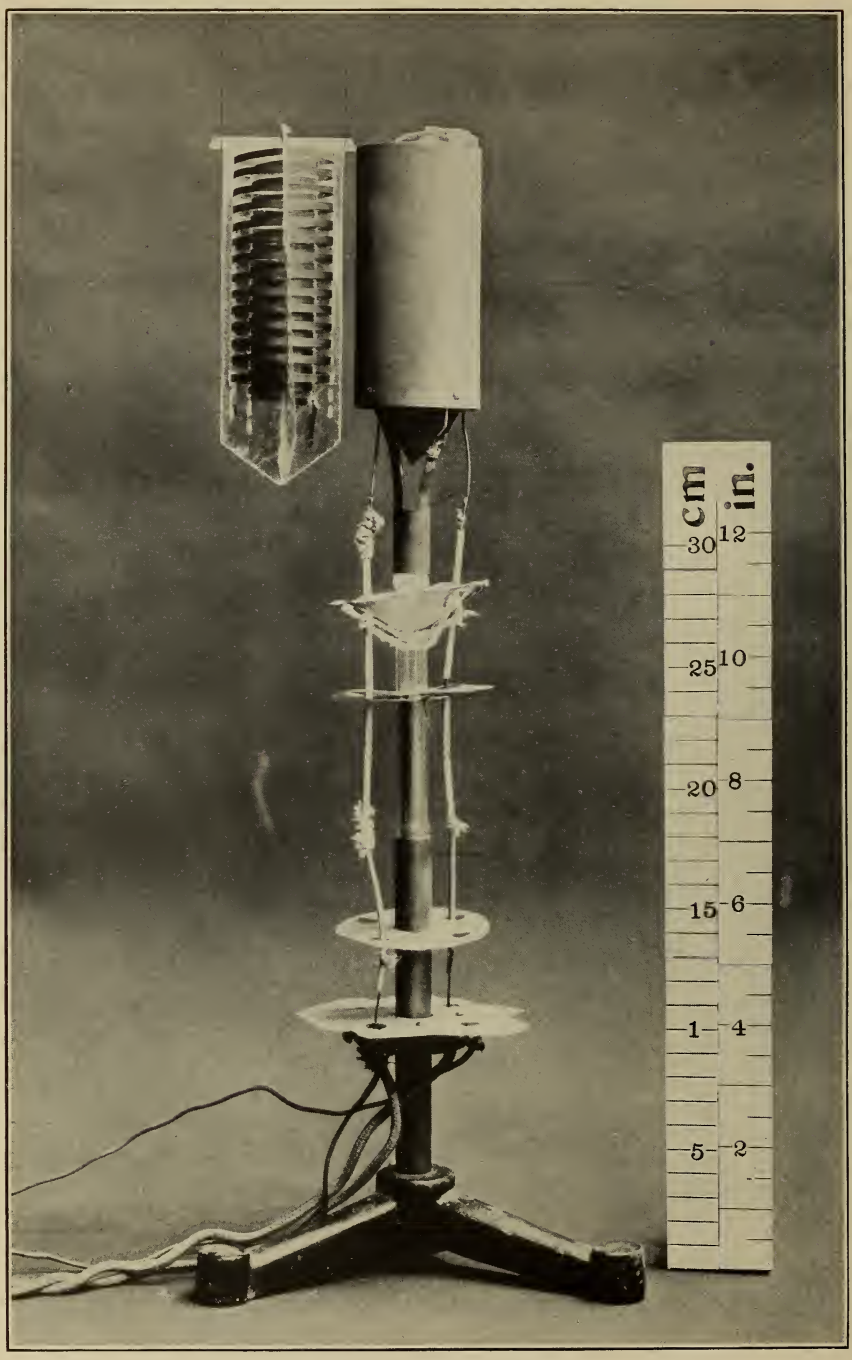


Fig. 10.—*Electric heating coil*

corrected readings is the relative change (at all points of the scale) which has occurred since the thermometers were certified. In the subsequent use of the thermometers, a so-called differential correction, to allow for this relative change, should be applied to the readings of one of the thermometers (preferably the outlet-water thermometer) in addition to the corrections given in the certificates.

3. HEAT LOSSES FROM CALORIMETER

Owing to various heat interchanges between the calorimeter and the surroundings, the observed heating value will, in general, differ from the total heating value of a gas by an amount depending upon the conditions prevailing during the experiment as well as upon the efficiency of the calorimeter as an absorber of the heat set free in the combustion chamber.

(a) **Efficiency of Calorimeter.**—Some idea of the efficiency of the calorimeter as a heat absorber may be obtained by supplying heat electrically within the combustion chamber at a known rate and observing how much of this heat is recovered in the stream of water flowing through the calorimeter. For this purpose the electric heating coil, illustrated in Fig. 10, was constructed. This coil consisted of a number of turns of nichrome ribbon, suitably insulated by mica, and provided with terminals to enable the potential difference between the proper points to be accurately measured. On the support for the coil was mounted a series of metal disks, as shown, to diminish the loss of heat through the bottom of the combustion chamber.

The expenditure of electric power in the coil was measured as follows: In series with the coil was connected a standard resistance (0.1 ohm), across the potential terminals of which the potential difference was measured by means of a potentiometer, the data so obtained serving for the calculation of the current through the heating coil. The other factor required, viz, the potential difference at the terminals of the heating coil, was determined by connecting the potential terminals of the coil to a 100:1 volt box, and then measuring the known fraction of the total potential difference by means of the potentiometer. The accuracy of calibration of the electrical apparatus was such that the measurements thus made should be reliable to at least 1 part in 10 000.

After the heating coil was placed in position within the calorimeter the electric current was regulated to give the desired expenditure of power in the heating coil, the flow of water through the calorimeter being so adjusted as to give the desired difference in reading between inlet and outlet water thermometers. The current was supplied by a 120-volt storage battery and remained very constant. The heating current was left on the coil for at least 45 minutes before beginning observations, to allow the attainment of equlibrium conditions. This was necessary on account of the considerable heat capacity of the coil supports.

During a known interval of time, usually three minutes, frequent readings were taken of the inlet and outlet temperatures of the water, the temperature of the air escaping through the products outlet, the current through the heating coil, and the potential difference at its terminals. The data summarized in Table 11 for one efficiency determination will serve to illustrate the method:

TABLE 11

Determination of Efficiency of Junkers Calorimeter No. 1209 by Electric Method

Mean inlet temperature of water, degrees centigrade	18.35
Mean outlet temperature of water, degrees centigrade	24.98
Mean temperature of escaping air, degrees centigrade	19.0
Mean temperature of room, degrees centigrade	18.0
Mean heating current through coil, amperes	10.839
Mean p. d. at terminals of coil, volts	47.86
Mass of water delivered in 180 seconds, grams	3360

The heat recovered in the water was

$3360\times(24.98-18.35)=22\,277$ calories (22° cals.)

$=22\,244$ calories (15°)

The energy expended in the heating coil was

$10.839\times47.86\times180.0=93\,376$ joules

$=22\,301$ calories (15°)

The efficiency of the calorimeter *as used*, when efficiency is understood to mean the ratio of the energy recovered in the water to the energy expended in the heating coil, is therefore

$$\frac{22\,244}{22\,301}=99.7 \text{ per cent}$$

The results of a number of such determinations on different calorimeters, made under different conditions as to rate of supply of electric energy to the coil and of flow of water through the calorimeter, are summarized in Table 12.

TABLE 12

Efficiencies of Flow Calorimeters by Electric Method

Date	Calorimeter	Determinations	Efficiency
			Per cent
November, 1910	Junkers No. 1209	15	99.8
July, 1912	do	4	100.0
September, 1911	Simmance-Abady, American type	3	98.9
October, 1911	Sargent	4	99.6
November, 1911	Simmance-Abady, English type	12	99.1–100.4
	do	7	99.7–100.3
	do	10	99.7
July, 1912	Hinman	10	99.9
October, 1911	Boys	2	96.0

As the accuracy of these tests is of the order of 0.2 or 0.3 per cent, it may be said that the efficiencies of the Junkers, Hinman, Sargent, and Simmance-Abady (English type) calorimeters as heat absorbers are practically the same, all being in excess of 99.6 per cent.

The low value found for the efficiency of the American type of Simmance-Abady calorimeter is undoubtedly due to the heat conducted away by the heavy metal tube which extends through the center of the calorimeter, and which is not in contact with the circulating water but is in good thermal communication with the heavy metal base of the calorimeter. The outer cylinder of the heating coil was very close to this tube, so that the efficiency may have been lower than with a Bunsen flame in the combustion chamber. In the Boys calorimeter the combustion chamber is so short that the heat losses from the base were very great with the heating coil used, which was not adapted to this calorimeter. The low efficiency found for this calorimeter, however, is in part corroborated by the low values obtained for the total heating value of illuminating gas.

The varying results obtained with the Simmance-Abady calorimeter are due to the fact that the perforated cone around the bulb of the outlet-water thermometer did not mix the water sufficiently to insure that the thermometer should indicate the true mean temperature of the effluent stream. When a suitable mixing device was substituted for the perforated cone supplied with the instru-

ment, more satisfactory results were obtained. The first series given in the table corresponds to determinations with the cone, the second series to determinations with no mixing device, and the third series to determinations with a baffle-plate mixer. Apparent efficiencies appreciably in excess of 100 per cent are due to errors in the indications of the outlet-water thermometer.

The meaning of such tests of the efficiency of a calorimeter has been often misinterpreted. As stated in the beginning of this section, such tests give an indication as to the proper design of the calorimeter (e. g., the sufficiency of heat-absorbing surface, of mixing of outlet water, etc.). However, when gas is burned in the calorimeter, the observed heating value is not the same proportion of the total heating value as is indicated by the efficiency as determined by the electric method; or, in other words, if the efficiency of a calorimeter had been found by the electric method to be 99.8 per cent, the observed heating values obtained with the calorimeter would not necessarily be equal to but might be very appreciably different from 99.8 per cent of the total heating value of the gas tested. The net heating value (uncorrected for heat losses) would, however, be approximately the same proportion of the true net heating value as is indicated by the efficiency determined electrically.

(b) **Surface Losses.**—The heat lost to the surroundings from the external surface of the calorimeter will depend upon the average excess of temperature of its surface above that of the surroundings, to some extent upon the physical condition of the surface as to polish, etc., and upon the condition of the air in contact with the surface, i. e., whether at rest or in motion. The heat loss from the surface may be considered under two heads, the loss due to the average excess of temperature of the surface of the calorimeter above the temperature of the inlet water, and a further loss (or gain) of heat due to the inlet water being above (or below) room temperature.

With gas burning in the combustion chamber of Junkers calorimeter No. 1209, the flow of water adjusted to give a 10° C rise in temperature, and the calorimeter shielded from drafts as usual, the temperature of the surface was measured at a number of points by means of a "surface thermocouple." This couple consisted of a fine constantan wire, the ends of which were soldered to

thin copper disks. A fine copper wire was also soldered to each of the copper disks, these wires serving as leads to a reversing switch which was connected to a galvanometer. One of the copper disks was mounted against the inlet water pipe, while the other was mounted against the part of the surface the temperature of which was to be measured. The disks were electrically insulated from the calorimeter by very thin sheets of mica. The disks, when pressed into intimate contact with the surfaces and loosely covered with cotton wool, must have assumed approximately the temperatures of the surfaces, and hence the electromotive force of the thermocouple was a direct measure of the excess of temperature of the one junction above that of the inlet water.

The thermocouple was calibrated by mounting one junction against the inlet water pipe and the other against the side of the outlet wier and observing the resulting galvanometer deflection. The temperature of the water in the inlet pipe and in the outlet wier was measured with thermometers. This method of calibration reduced the error due to the thermojunctions not being exactly at the temperatures of the surfaces with which they were in contact.

The average temperature of the various parts of the surface of the calorimeter was found to be higher than that of the inlet water by the amounts stated below:

The small cylindrical portion at the top (effective area 125 cm^2) was 5°.5 C warmer than the inlet water.

The upper conical surface (area 180 cm^2) was 4° C warmer than the inlet water.

The surface of the cylindrical body of the calorimeter (area 1450 cm^2) was 0°.9 C warmer than the inlet water.

The surface of the lower cylindrical portion (area 328 cm^2) was practically at the same temperature as the inlet water.

The 2100 cm^2 of the surface were therefore on the average 1°.3 C warmer than the inlet water, when the rise of temperature of the water flowing through the calorimeter was 10° C.

The rate of loss of heat from a polished nickeled surface, similar to that of the calorimeter, was determined by observing the rate of cooling of a nickel-plated closed can of known area and containing a known mass of water about 7° warmer than its surroundings.

These observations showed that the loss of heat was about 0.006 calorie per minute per square centimeter per 1° C difference in temperature. The rate of heat loss from the calorimeter, when the inlet water was at room temperature, was therefore $2100 \times 1.3 \times 0.006 = 16$ calories per minute. This corresponds to 0.064 Btu per minute for a temperature rise of 18° F of the water flowing through the calorimeter.

That this heat loss is comparatively unimportant may be seen from the following considerations: In a calorimetric measurement in which a gas of 600 Btu is burned at 7 cubic feet per hour, the rate of heat supply is about 70 Btu per minute. The loss of 0.064 Btu therefore amounts to a little less than 0.1 per cent. This heat loss, which is ordinarily called the "radiation loss," has been given an unwarranted importance in the literature of the subject, often being cited to account for large discrepancies found. In nonflow calorimeters of the usual types, where the total amount of heat measured is only 30 or 40 Btu in an experiment lasting 10 minutes or more, this loss is of far greater relative importance.

For calorimeters of similar construction (i. e., with the water passing through the calorimeter in but one direction, and having approximately the same area and a similar air jacket) the heat lost to the surroundings under the conditions discussed above will be approximately the same as for the Junkers calorimeter. For externally water-jacketed calorimeters, such as the Simmance-Abady, the loss will be less. This loss being so small for most flow calorimeters, it was not deemed of sufficient importance to warrant investigation for each calorimeter.

There will be further heat interchanges between the surface of the calorimeter and its surroundings if the temperature of the inlet water is above or below that of the room. The rate of this heat interchange was determined for a number of calorimeters by observing the change in temperature of water flowing through the calorimeter, with no gas burning, when the temperature of the inlet water was above, or below, room temperature by about 18° F. From the change in temperature of and the rate of flow of the water, this rate of heat interchange was directly computed. These rates of heat interchange for a number of calorimeters are given in Table 13.

TABLE 13

Rate of Heat Interchange Between Calorimeter and Surroundings, in Btu Per Minute per 1° F Difference Between Inlet Water and Room Temperatures

Calorimeter	Btu per minute per 1° F	Calorimeter	Btu per minute per 1° F
Junkers No. 1209, original type	0.022	Junkers No. 1443, new type	0.022
Junkers No. 876, original type	.024	Simmance-Abady, English type	.055
Hinman-Junkers No. 164	.034	Simmance-Abady, American type	.052
Sargent	.034	Boys	.034

If the surface loss of 0.006 calories per square centimeter per minute per 1° C difference of temperature is used to compute what the loss of heat from the Junkers (original type) calorimeter would be per 1° C difference between inlet-water temperature and room temperature, if the outer casing were removed, the loss is found to be about 10 calories per minute. (The effective area would be about 1700 cm^2 and $1700 \times 0.006 = 10$.) This loss is, however, precisely equal to the loss found per 1° C difference between inlet water temperature and room temperature for the calorimeter with air jacket; that is, the above data make it appear that the heat loss in still air is not decreased by the presence of the air jacket. The quantities of heat measured in these experiments were small, so that the above data were not determined with a very high degree of accuracy, and hence the conclusion from these data that the air jacket does not materially affect the amount of heat interchange between the calorimeter and the surroundings must be regarded as a first approximation. It is, however, probably true that the efficiency of the air jackets on these calorimeters has been overestimated. So far as is known to the authors no attempt has been made to verify experimentally the assumption that the air jackets materially reduce the heat losses from the calorimeters. However, it is probably true that the jackets do no harm, and they may be of advantage in reducing fluctuations in the amount of heat loss due to varying air currents.

In the Hinman-Junkers and Sargent calorimeters there is a long inlet water tube between the inlet-water thermometer and

the calorimeter for the purpose of bringing the inlet and outlet thermometers on the same level, a form of construction which probably accounts for the fact that the constant found is larger than for the Junkers calorimeter.

The effect of this heat interchange on a calorimetric measurement may be seen from the following considerations: Suppose the Sargent calorimeter were operated with the inlet water 5° F colder than the room, and a 600 Btu gas were being burned at 7 cubic feet per hour; the heat gained from the surroundings is $5 \times 0.034 = 0.17$ Btu per minute, which is 0.24 per cent of the heat (70 Btu per minute) furnished by the combustion of the gas. This, however, is not the only error introduced by operating the calorimeter with the inlet water below room temperature. Other errors due to this cause are considered on page 78.

It is obvious that, for a given calorimeter, the temperature of the inlet water may be so chosen that the sum of all *surface losses* (plus and minus) will be zero. For example, if the Junkers calorimeter No. 1209 were operated with the temperature of the inlet water 3° F below room temperature (no gas burning), it would gain $3 \times 0.022 = 0.066$ Btu per minute. Then, if gas is burned in the calorimeter so as to produce a rise of temperature of 18° F in the water passing through, there would be a rise in the average temperature of the surface sufficient to superimpose a loss of 0.064 Btu per minute, which almost exactly neutralizes the gain due to the inlet water being below room temperature. This result may also be stated as follows: If I be the temperature of the inlet water and O that of the outlet water, the calorimeter will interchange heat with its surroundings at the rate at which it would interchange heat if water at a temperature $I + {}^1/_6 (O - I)$ were flowing through the calorimeter with no gas burning (instead of $I + \frac{1}{2} (O - I)$ as has been assumed by some authors).

While the losses from the surface of the calorimeter may be eliminated by the method of compensation described above, the procedure is not to be recommended for several reasons; (*a*) it is easier to maintain the inlet water at room temperature; (*b*) the tables of corrections for atmospheric humidity (see p. 77) would not be applicable and, since the compensation would differ for different calorimeters, separate tables of corrections for atmos-

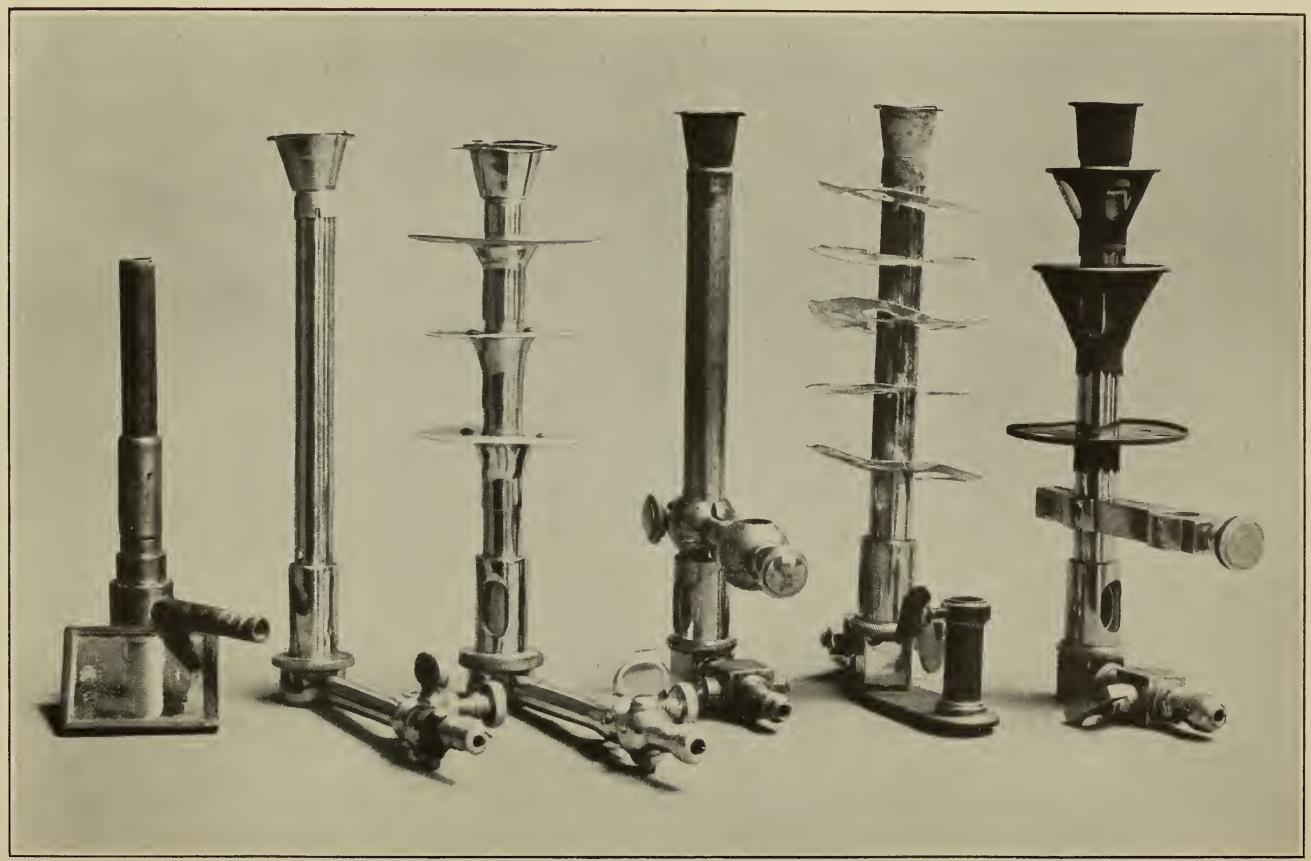


Fig. 11.—*Types of burners and radiation shields*

pheric humidity would be necessary for each type of calorimeter; (*c*) for most of the calorimeters included in these tests the surface heat loss, when the inlet water is at room temperature, is so small that it is inadvisable to modify the method of operation in order to compensate for the loss. The method of operating with the inlet water at room temperature is therefore preferable.

(c) **Position of Burner in Calorimeter and Use of Radiation Shields on Burner.**—Merely holding the hand under the bottom of the calorimeter when the burner is lighted makes it evident that some heat is being lost from the calorimeter. The amount of this loss will evidently depend to some extent upon the position of the burner; that is, it will be larger if the burner is set low, and may be diminished by raising the burner. The loss may be further diminished by mounting on the stem of the burner several radiation shields which may be made of thin polished metal disks perforated to admit air freely to the flame. Fig. 11 shows several burners equipped with various forms of radiation shields.

Position of Burner.—With most of the calorimeters tested, it was found that the burners were so mounted that they could not be inserted far enough into the combustion chamber. Thus, in the Junkers calorimeter (original type), while the heat loss was not sensibly diminished by raising the burner, it was found that even with the burner set as high as possible with the mounting furnished, the products of combustion were reheated several degrees Fahrenheit in the lower part of the calorimeter. When the burner support was modified, and the burner was raised about 1.5 inches higher and was provided with radiation shields, the products escaped from the calorimeter at a temperature not more than 0.5° F above that of the inlet water. No advantage resulted from further raising the burner. The reheating of the products has led many observers to underestimate the efficiency of the heat-absorbing system of the calorimeter and has also been the cause of some peculiar operating directions. As soon as the reheating of the products is eliminated it is at once evident why the escaping products must be saturated at or a little above the temperature of the inlet water, as was found by Immenkötter as the result of an extended investigation.

The effect that the position of burner may have on the resulting heating values is shown by the results given in Table 14 and which were found with Simmance-Abady calorimeters of the English and American types and with a Junkers calorimeter.

TABLE 14

Effect of Position of Burner on Heating Values

Date	Calorimeter	Position of burner	Heating values in Btu (without radiation shields)	
			Observed	Net
November 4, 1911	S.-A. English type.	Mounted on stand as furnished	655	.....
	.....do.....	Burner raised 3 inches	661	.....
November 10, 1911	S.-A. American type.	Burner mounted as furnished	695	639
	.....do.....	Burner raised 3 inches	706	646
May 22, 1913	Junkers No. 1209	Burner set as high as possible with mounting furnished.	647	598
	.....do.....	Burner set 1½ inches higher	648	599

It will be seen that the heating values found with the Simmance-Abady calorimeters were raised 1 per cent or more by raising the burner 3 inches.

Radiation Shields on Burner.—The use of radiation shields on the burner will raise the observed heating value by diminishing the sensible heat lost through the bottom of the calorimeter. The shields may also exert a slight influence in the direction of raising the observed heating values by returning to the inflowing current of air some of the heat that might otherwise be lost by conduction down the stem of the burner.

If a calorimeter were operated so that a considerable excess of air over that required for combustion was drawn through it, the addition of close-fitting shields with small openings might also raise the observed heating value by reducing the excess air supply, provided the air supply were still sufficient to insure complete combustion. The net heating value would not be affected, due to this cause. Such an effect, however, has not been observed with any of the shields used during the present series of experiments, the observed heating value being affected to practically the same extent as was the net value.

The results of a large number of experiments on the several calorimeters are summarized in Table 15. The experiments were made alternately with and without shields, all other conditions (except of course such change in air supply as was thereby caused) remaining the same in any one series of experiments. The table includes the results of some 150 determinations of heating values, and, with the exception discussed below, in no instance was the heating value with shields as low as without shields.

TABLE 15

Effect of Shields on Heat Losses

Date	Calorimeter and conditions of experiment	Gas rate, cubic feet per hour	Heating values, Btu		Increase due to shields, per cent
			Total	Net	
	Hinman-Junkers calorimeter No. 91:				
July 17, 1912	Without shields, damper open	12	670	616	0.7 in total
	With shields, damper open	12	675	620	0.6 in net
	Without shields, damper open	5.5	666	616	1.0 in total
	With shields, damper open	5.5	673	621	0.8 in net
July 18, 1912	Without shields, damper open	7	667	618	
	Heavy copper shields, damper open	7	671	621	0.6 in total
	Light aluminum shields, damper open	7	671	621	0.5 in net
	Without shields, damper open	7	667	618	
	Sargent calorimeter:				
Oct. 7, 1911	Without shields, damper open	4	676	.....	0.7 in total
	With aluminum shields, damper open	4	681	.....	
	Simmance-Abady calorimeter, English type (burner 3 inches higher than normal position):				
Nov. 7, 1911	Without shields, damper open	5	657	.....	0.6 in total
	With shields, damper open	5	661	.....	
	Simmance-Abady calorimeter, American type (burner 3 inches higher than normal position):				
Nov. 10, 1911	With shields, damper open	3	708	648	0.4 in total
	Without shields, damper open	3	706	646	0.4 in net
	With shields, damper open	3	709	649	
	Boys calorimeter:				
Sept. —, 1911	Without shields	4	644	.....	0.0 in total
	With 4 aluminum shields	4	643	.....	
	With 2 aluminum shields	4	645	.....	
	Junkers calorimeter No. 1209:				
Aug. 24, 1912	Without shields, burner very high, damper closed	7	701	646	0.6 in total
	With shields, burner very high, damper closed	7	705	649	0.5 in net

TABLE 15—Continued

Date	Calorimeter and conditions of experiment	Gas rate, cubic feet per hour	Heating values, Btu		Increase due to shields, per cent
			Total	Net	
	Junkers calorimeter No. 1209—Continued				
May 22, 1913	Without shields, burner very high, damper closed	7	657	.....	
	With shields, burner very high, damper closed	7	658	.....	
May 23, 1913	Without shields, burner highest position as furnished, damper closed	7	655	.....	0.2 in total
	With shields, burner highest position as furnished, damper closed	7	656	.....	
May 24, 1913	Without shields, burner as above, damper open	7	648	.....	
	With shields, burner as above, damper open	7	650	.....	
	Hinman-Junkers calorimeter No. 164:				
May 26, 1913	Without shields, burner highest position as furnished, damper closed	5.5	660	609	0.5 in total
	With shields, burner highest position as furnished, damper closed	5.5	663	612	0.5 in net
May 27, 1913	Without shields, burner 1½ inches higher than above, damper closed	5.5	652	601	0.2 in total
	With shields, burner 1½ inches higher than above, damper closed	5.5	653	601	0.0 in net
	Without shields, burner 3 inches lower than first position, damper closed	5.5	648	598	0.2 in total
	With shields, burner 3 inches lower than first position, damper closed	5.5	649	599	0.2 in net

The effectiveness of the shields in reducing the heat loss is perhaps best shown by the curves, Fig. 14, for observed and net heating values obtained with the Hinman-Junkers calorimeter No. 91, operated at different rates of gas consumption, which show that the heating values obtained with shields were about 0.8 per cent higher than those obtained without shields. For all the calorimeters, with the exception of the Boys, the heating values obtained with shields were higher than without them. The shields were not tried with the luminous flame burner furnished with the Boys calorimeter, but with a glass tube Bunsen burner which was substituted.

The experiments made in May, 1913, which were performed with extreme care under the most favorable conditions, showed that the effect of shields in diminishing heat losses is somewhat less than 0.5 per cent while all the earlier experiments indicate that the effect was 0.5 per cent or more of the total heating value. The results as a whole, however, show the advisability of using shields where high accuracy is sought.

(d) **Conduction Down Stem of Burner.**—The heat lost by conduction down the stem of the Bunsen burner is negligibly small, as may be seen from the following considerations: The area of that part of one of the burners furnished with the Sargent calorimeter, which was outside the calorimeter was estimated as about 40 cm^2. Using the figure already quoted (p. 54) for the heat loss from a nickeled surface per square centimeter per minute per 1° C excess of temperature above surroundings, namely 0.006 calorie, a simple computation shows that the average temperature of the exposed portion of the burner would have to be over 200° F before the loss would amount to 0.1 per cent for a 600 Btu gas, burned at 7 cubic feet per hour. The actual excess of temperature is very small.

(e) **Heat Carried Off By Products of Combustion.**—The products of combustion carry off from the calorimeter sensible heat, proportional to their mass and excess of temperature above that of the entering air and gas, and latent heat, equivalent to the latent heat of vaporization of the excess of water vapor carried out by the products over the water vapor carried in by the air and the gas.

If the calorimeter is operated at the normal rate of gas consumption (see p. 69), so that for illuminating gas (600 Btu) the ratio of volumes of gas to air is about 1 to 7, the amount of sensible heat carried off in the combustion products per 1° F excess of temperature during the combustion of 1 cubic foot of gas is about 0.1 Btu. As it has been shown that the temperature of the products can, in a properly designed calorimeter, be reduced very nearly to that of the inlet water by suitable location of the burner, it follows that the sensible heat carried away by the products may be made negligibly small.

The gas and air entering the calorimeter carry in an amount of water vapor determined by their volumes and their degrees of

saturation, and the products carry out an amount of water vapor determined by their volume and degree of saturation. The observed heating value will, therefore, differ from the total heating value on account of the latent heat carried off in the products, by an amount depending upon the degree of saturation of the entering air and gas and of the escaping products and upon their volumes.

The net heating value determined with the calorimeter will not, however, be affected in this way, as may be seen from the following considerations. The net heating value may be calculated from the total heating value by subtracting from the latter the latent heat of vaporization of the water formed during combustion. If any of the water formed during combustion is condensed in the calorimeter, the water so condensed may be measured and its latent heat of vaporization subtracted from the observed heating value, while the heat of vaporization of the remaining water formed by combustion, and which is carried off in the escaping products, does not appear in the observed heating value. If, for example, a large volume of dry air is drawn into the calorimeter a considerable amount of water vapor, formed in combustion, will be carried out by the resulting large volume of combustion products, and the observed heating value will be correspondingly low. However, a correspondingly smaller amount of water vapor will be condensed and collected, and the quantity to be subtracted from the observed heating value, to obtain the net heating value, will also be correspondingly diminished, so that the net heating value so found will be the same as if a smaller volume of air, or air of higher degree of saturation, had been drawn into the calorimeter.

Accurate determinations of the net heating value of a gas can therefore be made without a knowledge of the atmospheric humidity or of the volume of the entering air and of the escaping products. Experimental data corrobating this statement will be found under the section relating to atmospheric humidity, see p. 72.

Saturation of Entering Air.—The humidity of the air of the calorimetric laboratory was measured with an Assmann aspiration psychrometer,[10] Fig. 12.

Saturation of Gas.—It has been shown in the section on measurement of gas volumes that gas which has been passed through a

[10] Zs. für Instrumentenkunde, 12, p. 1; 1892.

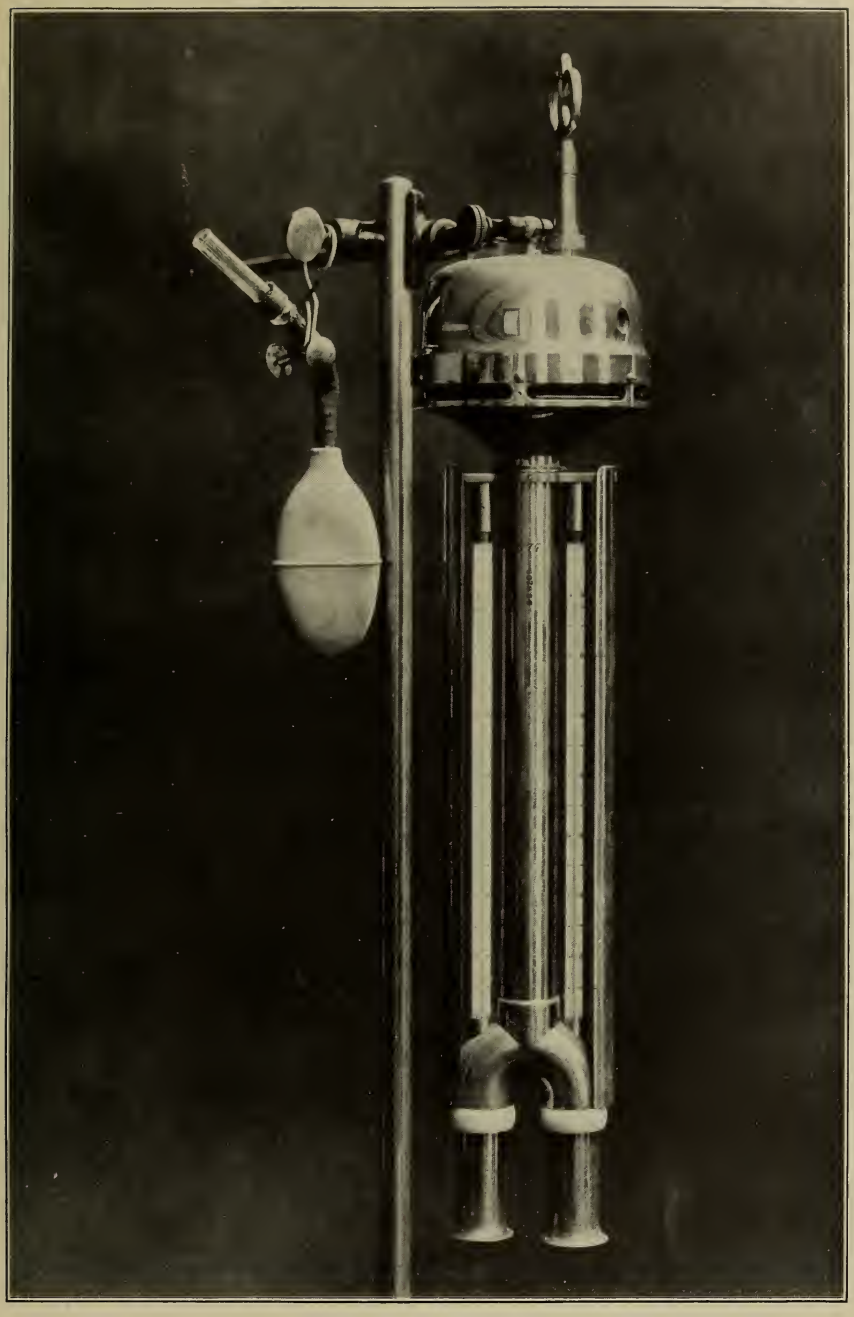


Fig. 12.—*Assmann aspiration psychrometer*

wet meter emerges saturated with water vapor at the temperature of the meter. Wet meters were used in all the experiments, so that the degree of saturation of the gas was always accurately known.

Saturation of Products.—Immenkötter has shown that the temperature at which the combustion products from the Junkers calorimeter are saturated is very approximately that of the inlet water. In the present experiments the saturation temperature of the products was measured by means of a dew-point hygrometer, consisting of a small externally silvered test tube containing mercury and a thermometer with its bulb immersed therein. Cooled mercury was poured into the test tube, the thermometer inserted, and the test tube held in the path of the escaping products. The dew point could be thus determined to an accuracy of about 1° F. In the earlier experiments with the Junkers calorimeter the products were reheated at the base of the calorimeter several °F before escaping from the outlet, owing to the burner not being set high enough. The saturation temperature of the products under these conditions was found to be from a few tenths to 1° F above that of the inlet water. The amount by which the observed saturation temperatures differed from inlet-water temperatures was almost within the limits of error of these experiments, although the small observed differences may have been real ones due to the reheated products taking up water vapor. In the later experiments, in which reheating of the products was avoided by modifying the burner support and raising the burner about 1.5 inches, the saturation temperature of the products must have been even more nearly equal to the temperature of the inlet water.

Volume of Entering Air and of Products.—If either the volume of the entering air or of the escaping products be known, and an analysis of the gas be available, the other may be determined. For the accuracy necessary for correcting observed heating values to total heating values, the following relations between these volumes may be used, assuming that the water formed in combustion is condensed to the liquid state:

If hydrogen is burned, volume of products = volume of air − 0.5 volume of hydrogen.

If illuminating gas is burned (550–650 Btu) volume of products = volume of air − 0.4 volume of gas.[11]

If natural gas (principally methane, CH_4) is burned, volume of products = volume of air − volume of gas.

In this investigation three methods of measuring the volume of air or of products were used (*a*) supplying air through a meter to the closed bottom of the combustion chamber, (*b*) determination of the volume of CO_2 formed by combustion of unit volume of the gas and analysis of CO_2 content of combustion products, and (*c*) measurement of velocity of combustion products through outlet tube of known area.

The arrangement for supplying measured volumes of air to the calorimeter is shown diagramatically in Fig. 15, and described on page 72.

In the products analysis method, the volume of CO_2 resulting from the combustion of a known volume of the gas was first measured and the percentage of CO_2 contained in the combustion products was next determined. From these data the volume of products was directly computed.

In the velocity of products method, it was necessary to use some instrument for measuring velocities, the use of which would not interpose sufficient resistance to appreciably change the velocity to be measured. For this purpose use was made of the fact that the *lag of a thermometer* in a gas varies with the velocity of the gas past its bulb. The details of the method need only be briefly outlined here, as the subject of thermometric lag has been fully treated in a paper by Dr. D. R. Harper 3d.[12] The method was applied as follows:

An extension tube about 8 inches long was fitted to the outlet products tube of the Junkers' calorimeter to insure greater uniformity of velocity of the products over the section of the tube, after their passage through the holes in the damper (when the damper was closed). The uniformity of velocity distribution was further promoted by mounting two small circular gauze diaphragms, about 0.5 inch in front of the damper opening, in such a way as not to appreciably obstruct the flow of the products. A

[11] Examination of a number of published analyses of illuminating gases of different character has shown that this relation may vary between the limits vol. products = vol. air − 0.2 vol. gas and vol. products = vol. air − 0.6 vol. gas. The former relation represents the smallest contraction of volume found for carburetted water gas, and the latter relation the largest contraction in volume found for coal gas.

[12] Bulletin, Bureau of Standards, 8, p. 659; 1912 (Reprint No. 185).

support was so arranged that a thermometer laid in it was in the axis of the extension outlet tube, the bulb being about 2 inches within the tube.

The calibration of this arrangement was made by passing air through the calorimeter at known rates, as measured by a gas meter previously calibrated at these rates, and determining the corresponding *lags* of the thermometer. The procedure was as follows: After the flow of air was started, the thermometer was placed in the support and left there for some minutes until its reading gave the temperature of the issuing air (water at room temperature flowing through the calorimeter kept this tempera-

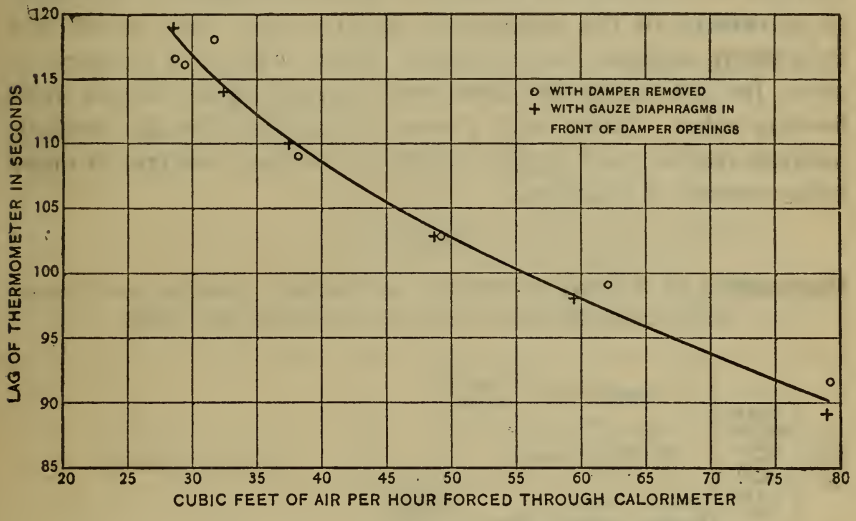


Fig. 13.—*Lag of thermometer No. 77874 vs. volume of air forced through Junkers calorimeter No. 1209*

ture constant); the thermometer was then warmed about 15° C by dipping into a beaker of warmed mercury and was then quickly transferred to the support above mentioned and, with the aid of a stop watch, the times were observed at which its readings were 10°.00 C and 3°.68 C, respectively, above the temperature of the issuing air. The time, in seconds, elapsing between these two readings of the thermometer is defined as the lag of the thermometer. A curve showing the relation between volume of air passing through the calorimeter and the lag of thermometer No. 77874, placed in the extension outlet tube, is shown in Fig. 13.

The operation of finding the volume of products escaping from the calorimeter under the conditions of use (i. e., gas burning and air drawn in by convective circulation) consisted in measuring the lag of the thermometer, in the manner just described, and in reading from the curve the corresponding volume of escaping products.

A large amount of data relating to the measurement of the volume of products escaping from the calorimeter, when air was drawn in by the action of the flame, has been obtained for a number of calorimeters under varied conditions of use, both by the products analysis method and the velocity of products method. The order of agreement of the methods is about 10 per cent, which is a sufficiently accurate determination of the volume of products to serve for correcting the observed heating value to the total heating value. Table 16 is a sample comparison of the products analysis method and of the velocity of products method of measuring volume of products.

TABLE 16

Measurement of Volume of Products by Products Analysis and Velocity of Products Methods, Junkers Calorimeter No. 1209

Experiment No.	Rate of gas consumption, cubic feet per hour	Values of Ratio $\frac{\text{Vol. products}}{\text{Vol. gas}}$				Conditions of operation
		By velocity of products			By products analysis	
		Thermometer No. 80659	Thermometer No. 77874	Mean		
1	7.1	5.9	5.7	5.8	5.7	Damper closed.
2	3.6	9.7	9.8	9.8	9.3	Do.
3	3.6	17.1	15.7	16.4	15.4	Damper open.
4	7.1	10.2	9.4	9.8	8.6	Do.

Under whatever conditions the calorimeter may be used, as to rate of gas consumption, damper opening, etc., provided that combustion is complete, it is possible, if the volume of the products, their humidity and that of the entering air be known, to apply the corrections necessary to reduce observed heating values to total heating values. Such data were obtained for a number of calorimeters. The results of a typical series for the Hinman-Junkers

calorimeter No. 91 are shown by the curves of Fig. 14. As appears from the curves, the rate of gas consumption was varied from 3 cubic feet to 12 cubic feet per hour, the calorimeter being operated with open damper. The volume of air varied from about 60 cubic feet per hour, for a gas consumption of 3 cubic feet per hour, to 85 cubic feet per hour for a gas consumption of 12 cubic feet per hour—i. e., increasing the gas supply four times—all other conditions remaining unchanged, increased the air supply by only about 40

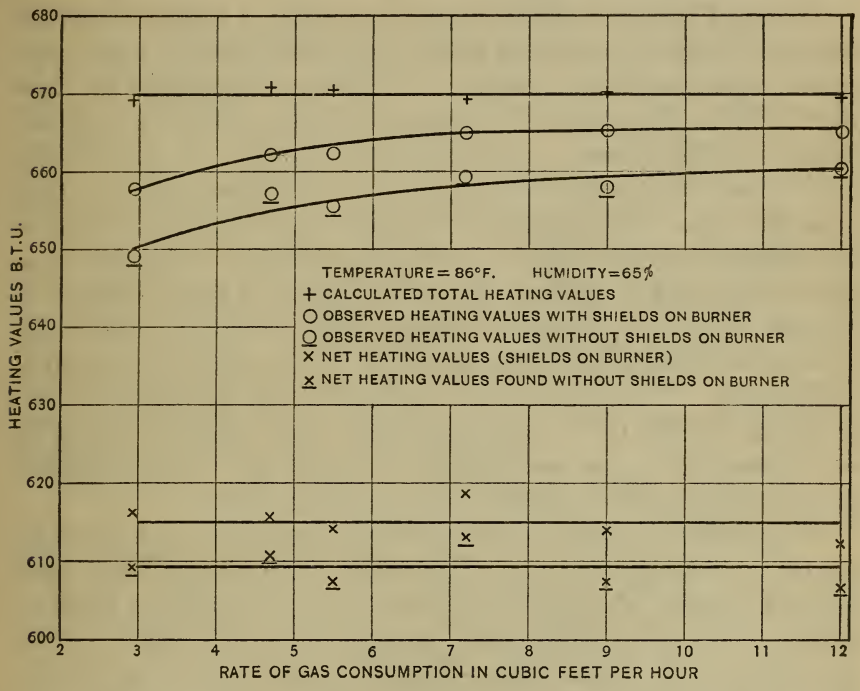


Fig. 14.—*Heating values found with Hinman-Junkers calorimeter No. 91, operated with open damper at various rates of gas consumption*

per cent, and most of this relatively small increase in air supply occurred at low rates (between 3 and 7 cubic feet of gas per hour). It appears from the above that at the low rate of gas consumption, a large excess of air was drawn into the calorimeter (ratio of volumes air to gas = 20), while at the highest rate only a small excess of air was drawn in (ratio of volumes air to gas = 7).

The method of correcting observed to total heating values is discussed on page 74. Fig. 14 shows that the various observed

heating values all lead to the same total heating value. The net heating values found are also in agreement to within the limits of experimental errors. Fig. 14 also shows the decrease in heat loss due to the use of radiation shields. That the increase in the heating values found with shields is not due to diminished air supply is shown by the fact that the net heating values are increased by the use of shields to practically the same extent as are the observed heating values.

Curves of the type shown in Fig. 14, giving a relation between observed heating values and rates of gas consumption, have been called *capacity-efficiency curves*. It is well to emphasize the fact that the form of these curves depends upon the conditions of operation of the calorimeter—e. g., whether the damper is open or closed, and if closed, the number of openings in the damper and their total area, and upon the humidity and temperature of the air at the time the experiments are made. If the experiments were made on a day of very high humidity, the curve would be a nearly horizontal straight line—i. e., observed heating values would be nearly the same at all rates of gas consumption up to the point of incomplete combustion. The lower values observed at low rates of gas consumption are due to the correspondingly high values of the ratios of volumes air to gas (and products to gas) and to the relatively greater importance of surface losses at the low rates.

Attention is directed to this matter for the reason that the committee on calorimetry of the American Gas Institute have published a number of capacity-efficiency curves for different calorimeters and have recommended operating the calorimeters at or near their point of maximum efficiency as shown by these curves. Thus, in the published curve for the Junkers calorimeter, this corresponds to a rate of about 7.5 cubic feet of gas per hour. The point which should be emphasized is that the curve referred to was obtained by operating the calorimeter with the damper closed, said damper having two openings, each 15 mm diameter. The capacity-efficiency curve of this calorimeter, operated with open damper, was found to be quite different from that obtained with the damper closed.

Fig. 14, as well as other data in this report, show that even at the maximum efficiency rate of gas consumption, the observed heating value will, in general, differ from the total heating value.

"Normal Rate" of Gas Consumption—Ratio of Air to Gas at the Normal Rate.—As will be shown in the following section, the correction from observed to total heating value is very simply made if the volumes and degree of saturation of air and of products be known, the magnitude of the correction depending upon the excess (or deficiency) of the water vapor carried out over that carried into the calorimeter. For the operation of calorimeters a suitable rate for the combustion of the gas, which will be called the *normal rate*, as well as the approximate values of the ratios air to gas and products to gas, may be found by the application of the following rule: Determine the rate of gas consumption at which combustion begins to be incomplete, and operate the calorimeter at 70 per cent of that rate. This will be the *normal rate* for the calorimeter and gas in question, for the conditions (damper opening, etc.) under which the calorimeter was operated.

The choice of the rate at which the calorimeter is to be operated is necessarily an arbitrary one. The rate of 70 per cent of that at which combustion begins to be incomplete was chosen for the following reasons: (*a*) At this rate the capacity-efficiency curves are approximately horizontal, so that the rate need not be very exactly fixed; (*b*) the rate is not so great as to make it probable that the combustion will be incomplete.

The rates for the different calorimeters, when determined by this rule, correspond approximately to those recommended by the committee on calorimetry of the American Gas Institute.

It has been found, both from products analyses and from measurements of the velocity of the products, that at the normal rate the volume of air drawn into the calorimeter is about 40 per cent in excess of that theoretically required for combustion as calculated from the chemical composition of the gas. For example, with an illuminating gas of about 650 Btu, the ratio of volumes air to gas at the normal rate of gas consumption is about 7 to 1; for natural gas of about 1000 Btu this ratio is about 12 to 1.

A convenient procedure for determining the rate at which combustion is no longer complete is as follows: With the calorimeter in operation, the rate of gas consumption is increased step by step, e. g., by successively increasing the load on the pressure regulator by adding weights. As long as combustion is complete,

the effect of increasing the gas rate is to cause an increment in the reading of the outlet-water thermometer. However, when the gas rate attains a value such that combustion is no longer complete, there will be a decrement in the reading of the outlet-water thermometer, accompanying an increase in the gas rate. The gas rate at which combustion begins to be incomplete (for a given damper setting, etc.) can thus be determined to within a few per cent. An almost equally good test is furnished by the odor of the combustion products, as the odor due to incomplete combustion is readily perceived for most gases.

To determine whether the normal rate was dependent upon the temperature rise of the water flowing through the calorimeter, the following experiments were tried: The Junkers calorimeter No. 1209 with damper closed, said damper having two openings, each 13 mm diameter, was operated so that the temperature rise of the water in successive tests was 14°, 25°, 36°, and 49° F, respectively. In each test the rate of gas consumption at which combustion began to be incomplete was determined in the manner already explained and was found to be approximately 8 cubic feet per hour for all of these temperature rises of the water. Hence the normal rate was independent of the temperature rise of the water in the calorimeter and was equal to $0.70 \times 8 = 5.6$ cubic feet per hour for the Junkers calorimeter No. 1209 operated with the special damper described above and with the illuminating gas (about 650 Btu) used in these tests.

If the facilities for making a gas analysis are available, the ratio of volumes products to gas may be determined for the normal rate of gas consumption by the method of products analysis previously referred to; but if such an analysis is not available, the method given above for determining the value of the ratio of volumes, air to gas, is sufficiently accurate for the purpose of reducing observed heating values to total heating values. That this is true has been shown by the data obtained in the intercomparison of a number of different gas calorimeters of the flow type. These intercomparisons showed that when the various calorimeters were each operated at their normal rate, as determined by the above rule, the total heating values obtained were identical, within the limits of experimental error; and, further, that the amount of water vapor

condensed and collected, per cubic foot of gas burned, was the same.

A further check on the applicability of the rule was obtained by means of the following experiment: Three dampers, each having two openings of 13, 15, and 17 mm diameter, respectively, were successively used with the Junkers calorimeter No. 1209. The results obtained in this experiment are given in Table 17.

TABLE 17

Junkers Calorimeter Operated at Normal Rates of Gas Consumption with Different Dampers

Damper used	Normal rate [13]	Water condensed per cubic foot of gas burned	Total heating value, Btu	Net heating value, Btu
	cu. ft. hr.	cc		
13 mm openings	5.5	21.0	656	606
15 mm openings	7	21.0	656	606
17 mm openings	8	21.2	658.5	607.5
Damper removed	10	20.8	656.5	607
			657	607

[13] Determined by the rule that normal rate = 70 per cent of rate at which combustion begins to be incomplete.

Further data in support of applicability of the method given for determining the value of the ratio of volumes, air to gas, was obtained from the following experiments. Illuminating gas of 650 Btu was burned in the Junkers calorimeter at the normal rate of 7 cubic feet per hour. The volume of products measured by the thermometer lag method was found to be 45 cubic feet per hour. The corresponding volume of air being 48 cubic feet per hour (i. e., $45+0.4\times7$) gave a ratio of volumes air to gas of practically 7 to 1. The gas required about 5 cubic feet of air per cubic foot of gas to furnish the oxygen necessary for combustion. The amount of air drawn in was therefore in this case very nearly 40 per cent in excess of that required. When natural gas of 1000 Btu was burned in the same calorimeter at a normal rate of 4.1 cubic feet per hour the ratio of volumes products to gas was found by products analysis to be 10.5 to 1, while computation (assuming 40 per cent excess of air at the normal rate) gave a ratio of 11 to 1.

The "maximum-efficiency" rates determined by the committee on calorimetry of the American Gas Institute with illuminating gas (about 600 Btu) for a number of calorimeters are practically identical with the normal rates for the same calorimeters, operated under similar conditions and with the same kind of gas. It is important, however, to call attention to the fact that neither the "maximum-efficiency" rate nor the normal rate are constants of the calorimeter, but vary with the conditions of operation (principally damper opening) and with the character of the gas burned (natural, illuminating, producer, etc.). The rule for determining the normal rate takes all these factors into account and gives sufficient information as to the values of the ratios air to gas and products to gas, so that the necessary corrections to obtain total heating values can be determined and applied. The normal rate can also be more simply and precisely determined than can the "maximum efficiency" rate.

(f) **Effect of Atmospheric Humidity.**[14]—In determining net heating values with a flow calorimeter, no account need be taken of atmospheric humidity. However, the observed heating value found will be affected by the humidity and volume of the entering air. This effect may readily be observed on a day of low humidity by opening the damper, when the observed heating value will be found to be lower than with the damper closed. The decrease in the observed heating value is due to the fact, that with the damper open, the air supply is increased, and more of the water formed by combustion is carried out as vapor in the escaping products.

The following experiments were devised to show quantitatively the effect of the humidity and volume of the entering air on the observed and on the net heating values. A diagrammatic sketch of the arrangement of the apparatus used is shown in fig. 15. A glass ring 2 inches high and 2.5 inches in diameter was fastened to the base of the Junkers Calorimeter with soft wax. This ring was closed at the bottom by a brass plate, through which extended the burner and a three-fourths inch tube to admit the air supply. The air was distributed within this cell by means of a cylinder

[14] The effect of atmospheric humidity on the results of heating value determinations with flow calorimeters has been considered for some special cases by Coste (J. Soc. Chem. Ind. 28, p. 1231; 1909) and by Parr (J. Ind. and Eng. Chem., 2, p. 337; 1910) and somewhat more generally by Holgate (J. Gas Lighting, London, 109, p. 355; 1910).

with gauze sides and closed at the top, and which fitted over the air inlet. A small inclined mirror on the brass plate was used for observing the flame. With the air distributor in position, the character of the flame was normal. Air taken from the laboratory pressure system was passed through a pressure regulator A, a meter B, a saturator C, consisting of a closed metal box with inlet and outlet tubes and containing water kept at a temperature of about 100° F by a burner, through a brass tube condenser D, containing brass turnings in its central tube, and supplied with water at room temperature from the thermostat, and thence into the

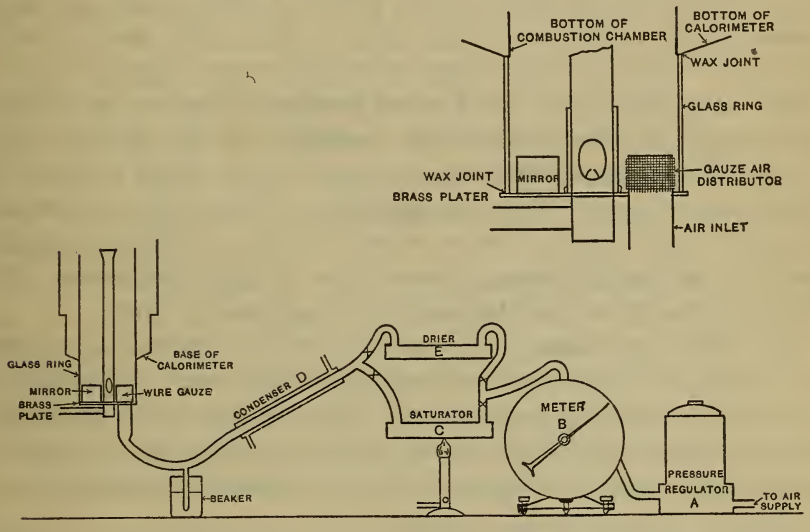


Fig 15.—*Arrangement of apparatus for supplying measured volumes of saturated or of dried air to a calorimeter*

calorimeter through the inlet tube described above. By means of this system air, saturated at inlet water temperatures, was supplied to the calorimeter. The saturator could be replaced by a drier, E, so as to supply to the calorimeter air of very low humidity and at inlet water temperature.

The results of a typical series of experiments are summarized in Table 18. In this table certain small constant corrections, such as those for heat losses from the surface, etc., which are applied in the reductions given on page 22, have been omitted, as they affect all the results equally.

TABLE 18

Effect of Volume and Humidity of Air on Heating Values, Junkers Calorimeter No. 1209 (Oct. 25, 1911)

Experiment No.	Gas burned, cubic feet per hour	Air supplied, cubic feet per hour	Humidity of air at 69° F.	Water, condensed, per cubic foot of gas burned	Observed heating value	Net heating value	Total heating value
			Per cent	cc	Btu	Btu	Btu
1	4.6	34.7	100	24.1	663.0	608	661
2	4.6	34.7	15	22.2	658.2	607	664
3	4.6	34.0	15	21.9	657.5	607	663
4	4.6	50.0	15	19.8	651.9	606	661
Mean						607	662

The table shows (*a*) that the net heating values are unaffected by changes in the amount and humidity of the entering air; (*b*) that when proper allowance is made for the latent heat of the water vapor carried off in the products of combustion, observed heating values obtained under widely varying conditions and differing considerably among themselves, all give the same total heating value to within the limits of experimental error.

The following example is given to show the method of calculation used in computing the correction which must be applied to the observed heating values to allow for the latent heat of vaporization of that part of the water which is formed in combustion and which is carried off as vapor in the products of combustion:

Example: Junkers calorimeter No. 1209.
Illuminating gas burned at normal rate=7 cubic feet per hour.
Temperature of room, meter, inlet water, and products=60° F.
Barometric pressure=30 inches.
Humidity of air=40 per cent.
Ratio of volumes air to gas=7.
Ratio of volumes products to gas=6.6.
Average temperature of outlet water=78° F.
Water vapor condensed and collected per cubic foot of gas burned=21.0 cubic centimeters.
Observed heating value=648.3 Btu.

1 cubic foot of saturated water vapor at 60° F weighs	0.372 grams.
Water vapor carried in by air per cubic foot of gas burned= $0.372 \times 0.40 \times 7$	=1.04 grams.
Water vapor carried in by 1 cubic foot of gas	= .37 grams.
Total water vapor carried in per cubic foot of gas burned	=1.41 grams.

Example—Continued

Water vapor carried out in products per cubic foot of gas burned=0.372×6.6 =2.46 grams.

Excess water vapor carried out per cubic foot of gas burned =1.05 grams.

Heat of vaporization of excess=1.05×2.3 =2.4 Btu.

Hence the heating value, corrected for the excess of water vapor carried out, is 648.3+2.3=651 Btu.

In the actual use of the calorimeter this computation need not be made for each observation, but the correction may be taken from Table 19 by entering the table with the arguments, temperature = 60° F, humidity = 40 per cent. Although in actual operation the equality of room temperature, meter temperature, inlet water temperature, and products temperature will not be exactly realized, the departure from this condition may be easily kept within limits such that no significant error will arise from the use of the table. This will be evident on inspection of the table, where it appears that the correction, for a given atmospheric humidity, changes rather slowly as the temperature changes.

In the computation of Table 19 the simple process used in the above example was modified to take account of the variation in the volumes of air, gas, and products, due to their water vapor content. Since it is the volume of products which is limited by the damper openings, the most reasonable assumption seemed to be that for the normal rate of gas consumption the ratio of volumes products to gas (rather than the ratio of volumes air to gas) would remain constant. The constant value taken for this ratio was 6.6, and the corresponding volume of air was calculated on the assumption that the volume of saturated air is given by the relation, volume of products = volume of air − 0.4 volume of gas. The simpler assumption made in the example given above, that both the ratios of volumes, air to gas and products to gas, are constant, is inconsistent, but would lead to no errors that are significant so far as the accuracy attainable with flow calorimeters is concerned. The tabular values are so calculated as to be directly applicable to observed heating values (where that term has the meaning assigned on p. 14) provided the measurements are actually made at a barometric pressure of 30 inches. If the measurements are made at a place where the barometric height,

H, differs considerably from 30 inches, the tabular corrections must be multiplied by the factor $\frac{30}{H}$ before being applied to the observed heating values. The tabular corrections are, however, directly applicable to heating values calculated to a temperature of 60° F and prevailing local barometric pressure.

The assumption that the relation between the volumes of air, gas, and products will be that used in computing this table, and that when gas is burned in the calorimeter at the normal rate the ratio of volumes, products to gas, will be equal to 6.6, are of course only approximately correct. The error in the first assumption would cause no appreciable change in the table. So long as the first assumption is valid any error in the second would not affect the correctness of the tabular values for 100 per cent humidity, but would affect the values for the lower humidities. For example, if the ratio of volumes, products to gas, were 7.6 instead of 6.6, the tabular correction for 40° F and 10 per cent humidity would be too small by less than 0.5 Btu, while the tabular correction for 90° F and 10 per cent humidity would be too small by about 2 Btu.

It is not probable, however, that under most conditions of testing the ratio of volumes products to gas would, when illuminating gas was burned at the normal rate, differ by much more from 6.6, than is assumed in the above example.

When the calorimeter was operated at normal rate of gas consumption and natural gas of high methane content (950–1000 Btu) was burned, it was found that the ratio of volumes products to gas was about 11 to 1 (the corresponding ratio of saturated air to gas being about 12 to 1). Table 20 is applicable to calorimetric determinations on natural gas under the same conditions as are stated above for Table 19 for illuminating gas.

In view of the ease with which the correction for effect of atmospheric humidity may be applied to observed heating values found with flow calorimeters operated at the normal rate, it seems inadvisable to complicate the apparatus by the addition of devices having for their object the saturation of the air entering the calorimeter, especially so since, even with a saturator, a correction to the observed heating value would still be necessary unless the air were delivered to the calorimeter at about 80 per cent saturation.

TABLE 19

Corrections, in Btu, to be Applied to Observed Heating Values in Calculating Total Heating Values of Illuminating Gas (about 600 Btu)

[The tabular corrections are applicable when inlet water, air, gas, and products are all at approximately the same temperature, and when the calorimeter is operated at *normal rate* of gas consumption (see p. 69).]

Temperature of room, etc.	Relative humidity of air									
	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
°F										
40	+ 2	+ 2	+ 1	+1	+1	+1	0	0	0	−1
45	+ 2	+ 2	+ 2	+1	+1	+1	0	0	0	−1
50	+ 3	+ 3	+ 2	+2	+1	+1	0	0	0	−1
55	+ 3	+ 3	+ 3	+2	+1	+1	+1	0	0	−1
60	+ 4	+ 4	+ 3	+2	+2	+1	+1	0	0	−1
65	+ 5	+ 4	+ 4	+3	+2	+2	+1	0	−1	−1
70	+ 6	+ 5	+ 4	+3	+3	+2	+1	0	−1	−2
75	+ 7	+ 6	+ 5	+4	+3	+2	+1	0	−1	−2
80	+ 8	+ 7	+ 6	+5	+4	+3	+1	0	−1	−2
85	+10	+ 9	+ 7	+6	+4	+3	+2	0	−1	−3
90	+12	+10	+ 9	+7	+5	+4	+2	0	−2	−3
95	+14	+12	+10	+8	+6	+4	+2	0	−2	−4

TABLE 20

Corrections, in Btu, to be Applied to Observed Heating Values in Calculating Total Heating Values of Natural Gas (about 1000 Btu)

[The tabular corrections are applicable when inlet water, air, gas, and products are all at approximately the same temperature, and when the calorimeter is operated at *normal rate* of gas consumption (see p. 69).]

Temperature of room, etc.	Relative humidity of air									
	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
°F										
40	+ 4	+ 3	+ 3	+ 2	+ 2	+1	+1	0	0	−1
45	+ 4	+ 4	+ 3	+ 3	+ 2	+1	+1	0	0	−1
50	+ 5	+ 5	+ 4	+ 3	+ 3	+2	+1	0	0	−1
55	+ 6	+ 6	+ 5	+ 4	+ 3	+2	+1	0	−1	−1
60	+ 8	+ 7	+ 6	+ 4	+ 3	+2	+1	0	−1	−2
65	+ 9	+ 8	+ 7	+ 5	+ 4	+3	+2	0	−1	−2
70	+11	+ 9	+ 8	+ 6	+ 5	+3	+2	+1	−1	−2
75	+13	+11	+10	+ 8	+ 6	+4	+3	+1	−1	−3
80	+15	+13	+11	+ 9	+ 7	+5	+3	+1	−1	−3
85	+18	+16	+13	+11	+ 9	+6	+4	+1	−2	−4
90	+21	+19	+16	+13	+10	+7	+4	+1	−2	−5
95	+25	+22	+19	+15	+12	+8	+5	+1	−2	−6

4. TEMPERATURE OF INLET WATER

It has already been mentioned that it is preferable to operate the calorimeter with the inlet water at the temperature of the room and to make corrections for the heat losses that occur under this condition of operation. If the temperature of the inlet water differs from that of the room, the conditions of heat interchange and the amount of heat carried off in the products of combustion will differ from what they would be if the inlet water were at room temperature. It is evident that if, with the calorimeter operated with inlet water at room temperature, the observed heating value is lower than the total heating value, it should be possible, by operating with the inlet water at some lower temperature, to obtain an observed heating value that should be identical with the total heating value. This method has been recommended by Parr [15] and has been extensively used elsewhere.[16] Parr, after giving an excellent analysis of the problem, unfortunately reaches the conclusion that, in using the Junkers calorimeter, the heat losses can be compensated under all conditions by operating the calorimeter with the inlet water at a temperature such that the exhaust gases leave the calorimeter at a temperature of 10° to 12° F below that of the room. In view of the importance given the subject, an extensive series of experiments to determine the effect of varying the inlet water temperature was made with two calorimeters, Junkers No. 1209 and Junkers No. 871, the latter kindly placed at the disposal of the Bureau for this purpose by Prof. O. L. Kowalke, of the University of Wisconsin.

Since the heat of combustion of a cubic foot of a given gas is a definite quantity, this value should be calculable from data obtained with the inlet water at various temperatures, provided corrections were made to take account of the following factors:

(*a*) Variation of the specific heat of water.
(*b*) Heat interchange with surroundings.
(*c*) Sensible heat carried off in products.
(*d*) Sensible heat carried off by condensed water.
(*e*) Latent heat of water vapor in products.

---

[15] J. Industrial and Engineering Chemistry, 2, p. 337; 1910.
[16] Report of Calorimetry Committee American Gas Institute, 1912.

In Fig. 16 are plotted, for a given sample of gas, the heating values obtained in a series of determinations with the Junkers calorimeter No. 1209, operated with the inlet water at various temperatures. The calorimeter was operated at the normal rate, so that the volume of products was approximately determined by this condition. It will be seen that the observed values, when corrected as indicated above, all lead to practically the same total heating value. Similar results were obtained with Junkers calorimeter No. 871. The point at which the observed heating

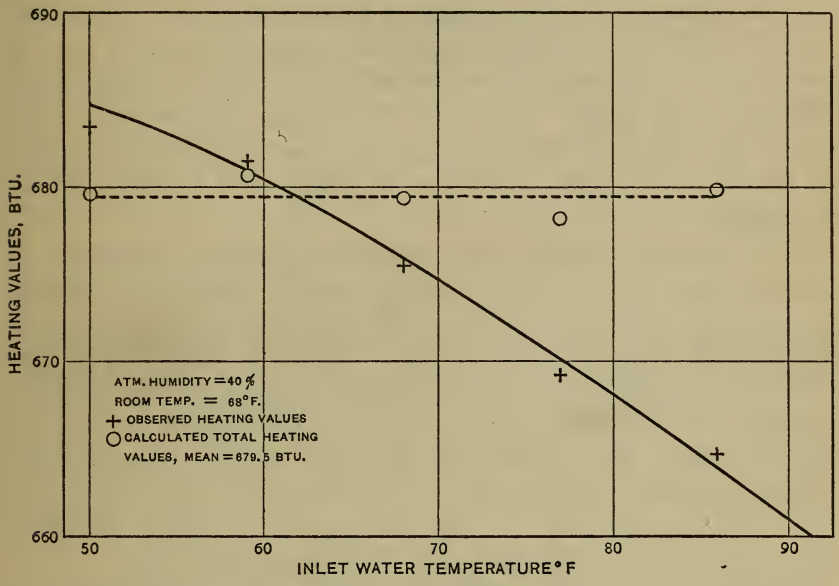


Fig. 16.—*Heating values found with Junkers calorimeter No. 1209, operated with inlet water at various temperatures*

value, under the conditions of humidity, etc., prevailing during this experiment, is the same as the total heating value is seen to be where the inlet water is about 6° F below the temperature of the room. As will be seen from the section on Effect of Atmospheric Humidity and from Table 19, conditions are possible under which it would be necessary to operate the calorimeter with the inlet water somewhat above room temperature, in order that the observed heating value should be identical with the total heating value. In other words, a constant difference of temperature between

exhaust gases and room temperature, as suggested by Parr, can not be used, but a table would have to be calculated giving the required difference for various degrees of atmospheric humidity and for different room temperatures.

An experiment made with a Simmance Abady (American type) calorimeter to determine the effect of operating with inlet water below the dew point of the surrounding atmosphere, indicated that there was no significant change at this point in the rate at which the calorimeter gained heat from the surroundings, although dew was deposited on the surface of the calorimeter. The above type of calorimeter was chosen for the test because its rate of interchange of heat with the surroundings, for a given temperature difference, was larger than for the other calorimeters. This matter was not further investigated, since calorimeters should not be operated under conditions in which dew is deposited on the surface.

It is evidently possible, by applying suitable corrections, to obtain correct total and net heating values from data obtained by operating a flow calorimeter with the inlet water at temperatures differing from that of the room. The correction to be applied to the total heating values on account of such difference of temperature will be different from that to be applied to the net heating values, due to the fact that part of the change in the observed heating value is due to a difference in the amount of water vapor condensed in the calorimeter, a factor which is eliminated in the determination of the net heating value.

The correction per 1° F difference between inlet water temperature and room temperature to be applied in the calculation of total and of net heating values will depend upon the room temperature. The corrections would be the same for all the calorimeters if it were not for the difference in the losses of heat from the surfaces. Since the effect of heat interchange with the surroundings is rather a small part of the total corrections, a table of corrections applicable without sensible error for all the flow calorimeters of the ordinary type may be computed by taking into account the five factors enumerated at the beginning of this section.

In Table 21 are given for various room temperatures the amounts per 1° F difference between room temperature and inlet-water temperature by which the total and the net heating values, calculated as if the inlet water had been at room temperature, must be corrected on account of such differences of temperature.

TABLE 21

Corrections per 1° F Difference Between Inlet Water Temperature and Room Temperature for Conditions Stated Above

Room temperature	Corrections in Btu for calculating total heating value	Corrections in Btu for calculating net heating value
°F		
50	0.5	0.4
60	.6	.4
70	.7	.4
80	.8	.4
90	.9	.5
100	1.0	.5

The corrections calculated from this table may be applied, without sensible error, to heating values of illuminating gas (about 600 Btu) determined with any of the flow calorimeters listed in this report (except the Doherty calorimeter), the correction being added if the inlet water is warmer than the room and subtracted if the inlet water is colder. The tabular values are average values for all the calorimeters, and are therefore slightly too large for the Junkers, Sargent, and Hinman-Junkers calorimeters and somewhat too small for the Simmance-Abady and Boys calorimeters. However, the error due to use of the tabular corrections will be unimportant for any of the calorimeters mentioned, for moderate differences of temperature (not over 10° F).

5. CONSTANCY OF FLOW OF WATER AND OF GAS; EFFICIENCY OF GAS PRESSURE REGULATORS

The effect on the readings of the outlet-water thermometers, due to variations (caused mainly by entrapped air) in the rate of flow of water through the calorimeter, has been considered on page 44.

Gas Pressure Regulators.—Two types of pressure regulators are in general use, the balance type and the float type, which are illustrated in Fig. 17. The former may be compensated for variable immersion. The latter was found to be satisfactory and was used throughout the present investigation. To obtain some idea of the efficiency of this type of regulator in reducing fluctuations of gas pressure, the following experiments were tried.

A meter, a regulator, and a burner were connected in series and the inlet pressure at the meter was varied from 1.5 to 6 inches of water. It was found that the amount of gas delivered (making allowance for the difference in pressure at which it was metered), as determined by timing the meter, was about 2 per cent less at the higher inlet pressure. The pressure maintained at the burner tip by the regulator was about 0.7 inch. The efficiency of pressure regulation may depend somewhat upon the amount of this pressure.

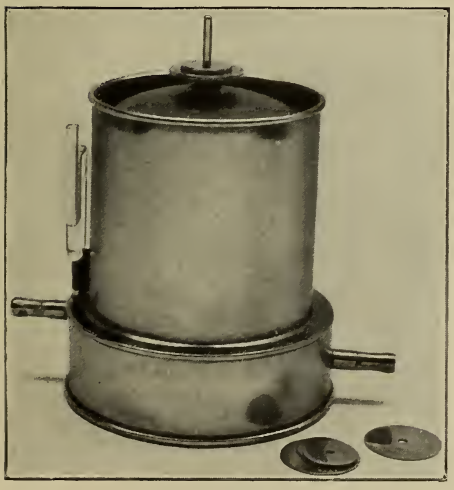
When two pressure regulators were used, one ahead of the meter and another between the meter and the burner, changing the inlet pressure on the first regulator from 1.5 to 6 inches of water produced a decrease of 0.5 per cent in the rate of gas delivery.

A series of experiments in which the weights on the regulator were removed and replaced, the float depressed, etc., while the pressure on the system was kept constant, showed that the regulator could not be relied upon to maintain a constant flow of gas over a considerable period of time to better than about 0.5 per cent. However, such variations of gas flow would introduce no serious error into a calorimetric measurement in which simultaneous measurements are made of the water flow and the gas flow.

If only one pressure regulator is used, it will usually be preferable to connect it between the gas supply and the meter rather than between meter and burner, as the inlet pressure at the meter will then be practically constant from day to day, and the small movements of the float, with their resulting variations in volume, will introduce no errors in the assumption that the volume of gas measured is equal to that burned.

If a float regulator of the usual type furnished with flow calorimeters is used, a difference in the position of the float amounting to one-sixteenth inch at the beginning and end of an experiment





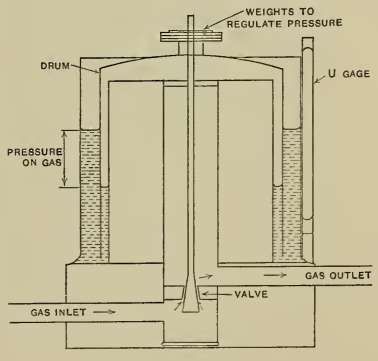


Fig. 17.—*Gas pressure regulators, balance and float types*

in which 0.2 cubic foot of gas is burned will cause an error in the result of about 0.3 per cent. It is therefore safer not to connect such a regulator between the meter and the burner unless the pressure at the meter inlet is kept constant, e. g., by another regulator, an arrangement which for several reasons is the most satisfactory.

The fluctuations in the readings of the outlet-water thermometer of the calorimeter were apparently no greater when the regulator was connected between the meter and the gas supply than when it was connected between the meter and the burner.

The experiments cited, as well as the results obtained in connection with the use of these regulators with calorimeters, show that such regulators will maintain the pressure sufficiently constant, so that no significant error will be introduced due to the effect of fluctuations of gas rate. The regulation is not sufficiently good, however, to warrant calculation of heating values from observations of the rate of water flow and of gas flow, instead of the usual procedure of determining the amount of water collected during the combustion of a measured volume of gas.

6. TIME REQUIRED FOR THE ATTAINMENT OF THERMAL EQUILIBRIUM IN FLOW CALORIMETERS

An essential condition for the correct measurement of heating values with flow calorimeters is that thermal equilibrium shall have been established before the measurements are begun, i. e., that none of the heat supplied during the period of observation shall go toward raising the temperature of any of the fixed parts of the calorimeter. It is evident that if a calorimeter is so constructed that any considerable mass of material, such as a metal chimney, is heated to a fairly high temperature during the operation of the calorimeter, the time required to attain equilibrium will be long. It is not true, as has frequently been supposed, that a large water content *necessarily* means that the calorimeter will require a long time to come to equilibrium, or will be slow in indicating changes in the heating value of the gas tested. A calorimeter of large water content will be slow in showing the effect at the outlet of changes in the temperature of the inlet water, or in coming to equilibrium if it initially contains water the temperature of which differs from that of the inlet water, the lag

being directly proportional to the water content and inversely proportional to the rate of flow of water. A method of reducing errors due to change in temperature of the inlet water is referred to on page 45.

To reduce to a minimum the time lag due to the fixed parts of a calorimeter, it is necessary that all parts which come in contact with the flame or with the heated products of combustion should be made of light material of high thermal conductivity and should be in intimate contact with the water flowing through the calorimeter. If the combustion chamber is made of sheet metal, one side of which is in contact with the water flowing through the instrument, the lag will be small (*a*) because the mass of metal to be heated is small, and (*b*) because the rise in temperature of this metal will also be small. If, however, the combustion chamber consists of heavy metal parts, as in the Boys and Simmance-Abady (American type) calorimeters, and the heat must be transferred from this metal to the water flowing in a pipe in poor thermal contact with these parts, a considerable quantity of heat will be absorbed by the metal before equilibrium is attained, and the lag will be correspondingly great. Insulating material which is slowly heated during the operation of the calorimeter will also increase the time required to attain thermal equilibrium. No indication was found that the use of radiation shields increased the time lag of any of the calorimeters tested.

While the accuracy attainable with a calorimeter of large time lag, under the most favorable conditions, is not necessarily less than that attainable with one of smaller time lag, the former will be very much less convenient and the results obtained with it in ordinary testing are subject to larger errors. The Junkers, Sargent, and Hinman-Junkers are examples of calorimeters of small time lag, while the Boys and Simmance-Abady (American type) represent a type having large time lag.

A convenient method of determining the time lag, is as follows: After the calorimeter has been in operation, i. e., with gas burning and water flowing at the usual rate (the inlet water being kept at constant temperature) until equilibrium has been established, the gas is shut off and the outlet-water thermometer read at frequent intervals until equilibrium is again established. In

Fig. 18 are shown, for different calorimeters, a number of curves which indicate graphically the results of such tests and the relative time lags of the various instruments. In these curves the portions corresponding to the first 8° C of temperature change, after shutting off the gas, have been omitted, so that the curves could be drawn to a more open scale. The form of curve found, for a given calorimeter, obviously may depend upon the rate of water flow and upon the rise in temperature of the outlet water at the time the gas was shut off.

When heating values are to be measured sufficient time should be allowed to elapse after lighting the burner and placing it in position within the calorimeter for the latter to come to an equilibrium condition in all its parts, before beginning observations. From the data represented graphically in Fig. 18, the conclusion was reached that with the Junkers calorimeter, observations may be begun three minutes after placing the lighted burner in position, without incurring risk of making an error exceeding 0.3 per cent due to the lag of the calorimeter. If a sudden change in the character of the gas or its rate of flow is such as to produce a total change in the outlet temperature of 2° F, it will take about 0.8 minutes for 0.9 of this change to take place and about 1.3 minutes for 0.95 to take place, i. e., the error that would result if observations were taken 1.3 minutes after such a change would be 0°.1 F, corresponding to an error of 0.7 per cent in the heating value (i. e., for a 15° F temperature difference). With the Boys calorimeter, under similar conditions, it would take about 10 minutes for 0.9 of the change to take place and about 15 minutes for 0.95 to take place, i. e., before the resulting error in heating value would be reduced to 0.7 per cent. To reduce the source of error under discussion below 0.5 per cent with the Boys calorimeter, the calorimeter should be placed over the lighted burner and fairly steady conditions should persist for 20 minutes before beginning observations. The lag of this calorimeter, as deduced from observations of the rate of cooling, may be somewhat greater than the lag corresponding to the heating up of the calorimeter, as was indicated by an examination of observations made under both conditions. The lag on heating up can not of course be as precisely determined as can the lag on cooling. The

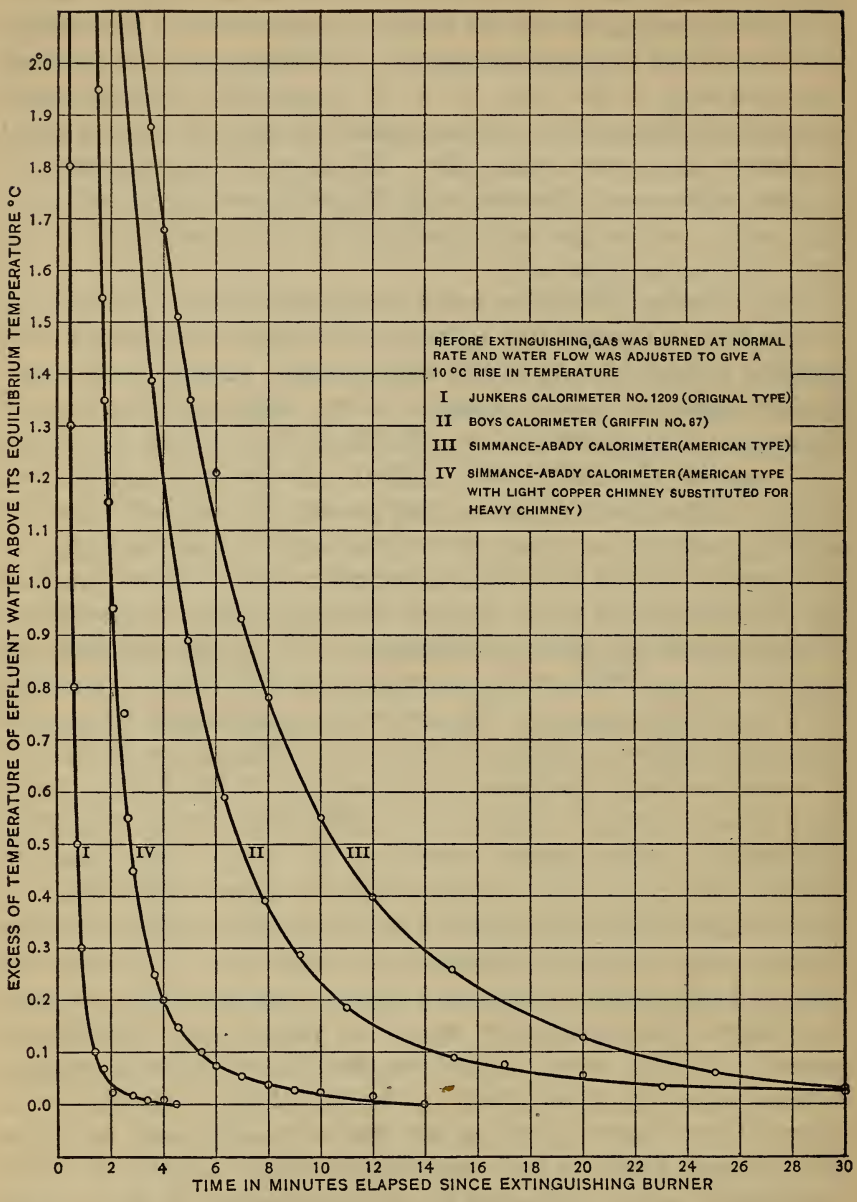


Fig. 18.—*Temperature-time curves for several calorimeters, showing the times required for attainment of thermal equilibrium after extinguishing burner*

statement made above for the Junkers would hold approximately for the Hinman-Junkers and Sargent calorimeters. The Simmance-Abady (American type) calorimeter should be allowed an even longer time than the Boys calorimeter to attain a steady state, before beginning observations, on account of the heavy metal chimney surrounding the burner and in contact with the metal base of the calorimeter.

7. MEASUREMENT OF WATER CONDENSED IN CALORIMETER—NET HEATING VALUE

For the accurate measurement of the amount of water condensed in the calorimeter per unit volume of gas burned, it is essential: (*a*) that there should be no leakage of the water flowing through the calorimeter into the spaces where the water formed in combustion is condensed and collected; (*b*) that the drainage of the condensed water should be uniform. If there are any leaks in the flues, etc., accurate determinations of net heating values are impossible. Uniformity of drainage is promoted by: (*a*) proper shaping of surfaces and ends of tubes, etc; (*b*) uniform wetting of the surfaces. The calorimeter should be operated for a sufficient length of time, before beginning measurements, for the surfaces to become wetted and the drainage therefrom to become uniform. The drainage should not take place from a water surface of large area, as very slight variations in the height of such a surface due to capillarity may cause irregularities in the amount of water collected.

It was found that in a properly designed calorimeter, the amount of water condensed (about 20 cc) during the combustion of a cubic foot of gas did not vary more than about 0.5 cc, in a series of six successive experiments. While at times the error may be somewhat larger than 0.5 cc, it will rarely be necessary to collect the condensate resulting from the combustion of more than a cubic foot of gas, as an error of 1 cc in the amount collected would result in an error of only 2.3 Btu in the net heating value. The amount collected during the combustion of 1 cubic foot of gas is sufficient to render negligible the irregularity due to the fact that the condensed water is discharged in drops (which are rarely larger than 0.1 cc) instead of in a continuous stream. A 25 cc

graduate is suitable for the collection and measurement of the condensed water.

The condensate collected during the time that the meter makes a given number of revolutions corresponds to a certain volume of gas measured under the prevailing conditions of temperature and pressure, etc. If the gas volumes are corrected to standard conditions, the amount of condensate collected must be divided by the same factor used in reducing gas volumes, to find the amount condensed per cubic foot of gas measured under standard conditions. The net heating value is then obtained by subtracting from the observed heating value, the heat of vaporization of the condensed water, and applying other necessary corrections (for heat interchange).

Heat of Vaporization of Water.—The heat of vaporization of water at the temperatures at which calorimetric experiments are usually performed is approximately 2.3 Btu per cubic centimeter or per gram (the difference between expressing the amount in cubic centimeters or in grams being negligible). The constant often used, 2.4 Btu per cubic centimeter corresponds more nearly to the heat of vaporization at 32° F. Since the temperature coefficients of the reactions occurring in combustion are neglected, it is undesirable to use for the heat of vaporization a value not applicable to the temperature of the experiment. The value 2.3 Btu per cubic centimeter should therefore be used for the heat of vaporization of water in the reduction of observations made with flow calorimeters under ordinary conditions.

8. MANIPULATION OF CHANGE-OVER DEVICE

The precision attained in operating the change-over device so as to divert the water from drain to weighing bucket and vice versa at the exact instant the meter index passed through the zero position was tested as follows:

The change-over device (in this case a split funnel mounted on a rotating arm between two stops) was made to operate an electric contact device in circuit with a chronograph. At the instant of passage of the hand of a stop watch through its zero position, as estimated by the operator, he shifted the change-over device, thus causing the time of shifting to be registered by the chronograph.

When the hand of the stop watch again passed through its zero position, the change-over device was shifted back, the exact time of which operation was again registered by the chronograph.

The interval of time that actually elapsed between the operations of shifting the change-over device over and back again was thus found not to differ on the average from the interval the operator had intended to include between these two manipulations by as much as 0.2 second, the difference only occasionally attaining 0.5 second. The error in judging the time of coincidences between index and graduation is probably smaller for the meter (7-inch dial) than for the stop watch (1.5-inch dial). The magnitude of the error that may be caused in a calorimetric determination, due to error in manipulation of the change-over device, may be seen from the following considerations·

If a flow calorimeter is used, in which gas is burned at the rate of 6 cubic feet per hour, and 0.2 cubic foot of gas is burned in a test, the time that elapses between the two operations of shifting the change-over device from drain to bucket and back again is 120 seconds, and as the time interval may be in error by 0.5 second, the corresponding error in the amount of water collected, and hence in the resulting heating value, for any individual determination may attain about 0.4 per cent, although on the average it would be less than half that amount.

The figures given above for the errors of manipulation of the change-over device, dependent as they are upon a number of factors such as the variation in the reaction time of the operator, his skill and experience in such manipulations, etc., would undoubtedly vary with different observers, with the rate of motion of the meter index, with the care taken to avoid parallax, etc. The data given are, however, sufficient to show that the error introduced into a heating value determination by the errors incident to manipulation of the change-over device are no greater than unavoidable errors made in other operations involved in the determination. It is evident that no systematic error is likely to be introduced, unless the two operations of shifting from drain to weighing bucket, and back from bucket to drain, require considerably different manipulation.

The Sargent calorimeter is provided with an automatic change-over device (Fig. 23), the meter index closing an electric circuit when passing through its zero position, thereby energizing an electromagnet, the armature of which is arranged so as to release a dumping bucket. When properly made, such a device reduces the error in the time of shifting to a negligible amount. The contact device must be so made as not to interfere with the proper operation of the meter.

9. WEIGHING OR MEASURING THE WATER

No appreciable error need be introduced in weighing or measuring the water. A Rueprecht 15-kg balance was used in these tests. It was considerably more sensitive than required for the work. A convenient type of balance used with these calorimeters is shown in Fig. 22. The balance is in equilibrium with the empty calorimeter pail in position as one pan of the balance. With such balances weighings can be conveniently and quickly made to an accuracy of a few thousandths of a pound, which is in excess of the required accuracy, as the amount of water to be weighed is usually over 6 pounds.

It is best to have the weights standardized before use. The balance should be tested at occasional intervals for equality of arms by interchange of weights on the balance pans. In a properly designed and well-made balance shifting the position of the weights on the pan should cause no significant change in balance.

In work of high precision with the bomb calorimeter it is customary to reduce all weighings to weight in vacuo. In reducing the observed weight of water to weight in vacuo the observed weight would be increased by approximately 0.1 per cent. This correction can therefore be neglected in gas calorimetry. The correction, however, has been applied in these tests partly from force of habit and partly on the principle of taking into consideration all corrections amounting to 0.1 per cent.

It is good practice to wipe dry the inner wall of the weighing bucket at the conclusion of one test and before beginning the next. However, if the water is simply poured out and the can shaken vigorously while in an inverted position, the amount of water that will remain clinging to the walls will not exceed 1 gram (0.002 pound) for a can with bright tinned inner surface and 3

grams for an oxidized copper or laquered inner surface, corresponding in the worst case cited to an error of 0.1 per cent in the observed heating value.

The small corrections for variation in the specific heat of water with temperature are considered on page 11.

Some calorimeters are furnished with glass graduates for measuring the volume of water instead of weighing it. Such graduates are sometimes made in the form shown in Fig. 30, having an enlargement at the bottom and with only the upper cylindrical portion graduated, thus giving a more open scale in the region actually used without unduly increasing the length of the graduate. If such graduates are carefully standardized, volumes can be readily measured in this way to within 0.1 per cent.

To allow for the combined effects of the variation with temperature of the specific heat of water (for a temperature rise of 15° to 20° F) and the thermal expansion of the water and of the graduate, the observed volumes should be multiplied by the factors K, for temperatures T, as given in Table 22, where T is the temperature of the outlet water, in order to obtain the equivalent mass of water at 15° C (or at 60° F). An additional correction must be applied if the volume of the graduate at 60° F is in error.

TABLE 22

Factors for Reduction of Volumes of Water Measured at T° to Equivalent Mass of Water at 15° C (or at 60° F)

[Multiply observed volume by factor K]

T	K	T	K
°F		°C	
60	1.001	15	1.001
70	0.998	20	0.998
80	.995	25	.996
90	.993	30	.994
100	.991	35	.992
110	.989	40	.991
		45	.989

It will be seen that, when volumes are measured and the temperature of the outlet water is high, this correction is too large to be neglected.

Evaporation of Water.—The error due to loss of water by evaporation between the time the water leaves the calorimeter and the time the weighing or measuring is done was found to be always negligible. Water may be lost by evaporation, either while the water is flowing from the calorimeter into the measuring vessel or by evaporation from the surface of the water in the vessel. The amount lost while the water was flowing could not be directly measured, but was estimated from thermal data, as follows:

The calorimeter was operated in the usual way, so that the average temperature of the outlet water was about 100° F, the room temperature being 82° and the humidity 63 per cent. The average reading of the outlet-water thermometer during the two minutes that the water was flowing into the weighing bucket was determined, and the temperature of the water in the bucket determined immediately afterwards with the same thermometer. After correcting for the loss of heat from the bucket and for the heat required to raise the temperature of the bucket the total decrease in temperature of the water was found to be less than 0.3° F. The evaporation of 0.1 per cent of the water would lower the temperature of the remainder by about 1° F if all the heat required for evaporation were supplied by the water. The loss of weight by evaporation under the conditions of the experiment, while the water was flowing, was therefore certainly less than 0.03 per cent. Under conditions of lower relative humidity the evaporation might be two or three times as much for the same temperature, but would hardly ever amount to 0.1 per cent. The amount of evaporation will depend upon the change-over device, etc., in use and could readily have been diminished if necessary. The loss of weight by evaporation from the weighing bucket was found, by a series of weighings extending over several hours, to be entirely negligible in the time required for a test.

10. MEASUREMENT OF VOLUME OF GAS

The sources of error that may affect the measurement, by means of wet meters, of the volume of gas burned in a calorimetric test, the precautions to be observed in the use of these meters, and the accuracy attainable in their standardization and use, have been considered in detail in Section VI, relating to "Measurement of the gas volumes," page 23.

11. LEAKAGE OF GAS

The gas meter and the gas connections between the meter and the burner must be free from leaks, and tests for leakage should be made at frequent intervals. The test may be conveniently made, if there is a stopcock at the inlet of the burner, by closing this cock with the gas pressure on, and noting whether there is any appreciable movement of the meter index during an interval of 5 or 10 minutes. If there is no stopcock, the tubing may be disconnected from the burner and a plug inserted in the end of the tube, and the test made as above. The possibility of a leak beyond the point at which the gas is shut off should not be overlooked. The leakage should be made so small that its amount, in the time required for a test, is entirely negligible (less than 0.0001 cubic foot if 0.2 cubic foot of gas is burned in the test). The gas pressure should not be left on the meter except when operating the calorimeter, or when making a leakage test, since so doing may cause a leakage of water through the stuffing box of the drum shaft, which would result in lowering the water level in the meter, thus necessitating more frequent readjustment of the water level.

12. MEASUREMENT OF ATMOSPHERIC PRESSURE

An error of 0.1 inch in the barometer reading will cause an error of 0.3 per cent in the calculated heating value. A barometer should therefore be used, the readings of which are reliable to 0.02 or 0.03 inch. Since the density of mercury and the length of the barometer scale are both affected by the temperature, it is necessary to reduce observed barometer readings to standard conditions; i. e., to the height in inches of the mercury column if the mercury were at 32° F (0° C). Tables for making such reductions, which take into account the variation in length of the scale of the barometer and the variation in the density of mercury with temperature, are readily obtained. The thermometer used for determining the mean temperature of the barometric column is usually mounted on the barometer. The error in heating value due to neglecting entirely the temperature correction of the barometer may attain 0.6 per cent (at a temperature of 95° F). In addition to the temperature corrections, it may be necessary to correct the observed barometer readings to allow for the effects of

(*a*) depression of meniscus if barometer tube is of small bore;[18] (*b*) pressure of any gas that may be above barometric column;[19] (*c*) index error and scale error;[20] (*d*) variation from standard gravity.[21]

If the laboratory has a fairly constant temperature (within 10° F) throughout the year, the total correction to be applied to the barometric readings, to allow for the combined effects of all the corrections mentioned above, may be determined once for all, either by evaluation of the individual corrections, or more conveniently, by comparison with a standardized barometer. Under these circumstances, a pressure regulator may be connected between the gas supply and the meter and the inlet pressure on the meter may be adjusted, provided the pressure of the gas supply is always sufficient, so that the excess of pressure in the meter, above atmospheric pressure, is equal and of opposite sign (since the temperature correction is the principal one) to the sum of all the barometric corrections, in which case the pressure of the gas in the meter will be given directly by the reading of the barometer.

For example, the temperature of the laboratory in which the present experiments were made averaged about 82° F, during a considerable part of the year. The total barometric correction for this temperature was −0.15 inches. The inlet pressure on the meter was therefore made equal to 2.1 inches of water, so that the uncorrected barometric reading was equal to the pressure of the gas in the meter. This method of compensating for the

[18] If the bore of the barometer tube is small, the pressure of the mercury meniscus may be sufficient to depress the barometric column by an amount that is significant. Thus in a tube of one-fourth inch bore, the depression may attain 0.05 inch. This source of error may be oviated by avoiding the use of a barometer tube of bore as small as one-fourth inch. The meniscus correction is discussed in Bureau of Standards Circular No. 46.

[19] In a barometer that has been filled with proper care, the trace of air above the mercury column should be so small as to exert no significant pressure. In most barometers the presence of air can only be detected by comparisons with a standard barometer at various pressures. In a primary standard barometer the effect of residual gas can be determined by measuring the same pressure with the upper mercury meniscus at different parts of the tube.

[20] In a barometer in which the position of the lower mercury surface is fixed by an index, the setting of the index, with reference to the graduated scale may be in error, in which case a correction for index error is necessary.

[21] Since gravity varies from place to place and with the altitude of the station, the pressure exerted by a barometric column of specified height will also vary. This correction varies from practically zero in the most northern latitude of the United States to about 1 part in 600 of the observed barometric height in the most southern latitude. The correction for variation of gravity with altitude is entirely negligible in gas calorimetric measurements.

barometric corrections is evidently not applicable if the sum of these corrections has a too small negative, or a positive value.

13. EFFECT OF USING FRESH WATER IN GAS METER

It is well known that water will absorb in different degrees the various constituent gases that enter into the composition of illuminating gas. The rate of absorption will evidently depend upon the degree of saturation of the water by each constituent, being greater if the water is fresh. The effect of absorption manifests itself in two ways: (*a*) in causing an error in the measurement of volume; (*b*) in changing the heating value of the complex mixture by selective absorption, so that the composition of the gas delivered, after passage through the meter, is different from that entering the meter. An idea of the magnitude of the effect is given by the results in Table 23. The meter having been filled with fresh water, the observed heating values recorded in column 3 were found after the amounts of gas recorded in column 2 had passed through the meter.

TABLE 23

Effect of Use of Fresh Water in Meter on Observed Heating Value

[Junkers calorimeter No. 1209. Gas rate=5.5 cubic feet per hour]

Time	Volume gas passed through meter since filling with fresh water	Observed heating value of gas
h. m.	cu. ft.	Btu.
4 13	0.5	656
4 16	0.8	657
4 24	1.5	659
4 27	1.8	658
4 46	3.5	659
4 49	3.8	660
5 02	4.9	659
5 05	5.2	659

It will be seen that the effect, due to the use of fresh water in the meter, on the observed heating value of this sample of illuminating gas was of the order of 0.5 per cent and that the water had become practically saturated, so far as calorimetric measure-

ments are concerned, after the passage of 2 or 3 cubic feet of the gas.

An experiment was arranged to determine directly the effect of any possible absorption of the constituents of the gas by fresh water. For this purpose two meters were joined in series, one being filled with water saturated with the gas, the other with fresh water. The water in both meters was at room temperature. The ratios of the volumes of gas indicated by the two meters was then determined immediately after the gas was first turned on and at intervals thereafter until about 10 cubic feet had been passed. To determine whether the fresh water was still absorbing gas, the gas was then passed through the meters in the opposite direction and the same value was found for the ratio of volumes indicated by the two meters. These experiments showed that the absorption of gas in the meter filled with fresh water did not exceed 0.2 per cent, even at the start when only a half cubic foot of gas had been passed through the meters. The same result was found in two such experiments, in one of which the gas was passed first through the meter containing the fresh water and in the other of which the gas was passed first through the meter containing the saturated water.

Any effect on the observed heating value due to absorption of gas by the water in the meter may, therefore, be avoided by running several cubic feet of gas through the meter, after filling it with fresh water.

14. EFFECT OF USE OF NEW RUBBER TUBING

It is known that the absorption of constituents of illuminating gas by rubber tubing through which the gas is passed may cause a measurable change in its properties. To accentuate any such effect, an experiment was arranged as follows: Gas from the holder was led to the meter through a short length of rubber tubing. From the meter the gas was passed to the regulator and thence to the burner through either of two circuits, in one of which was about 5 feet of old rubber tubing that had long been in contact with gas, while in the other circuit a 33-foot length of new rubber tubing, which had never been in contact with gas, was included. A series of heating value determinations was then made from time

to time with the gas taken alternately through these two circuits. The results of these experiments are shown by the curves, Fig. 19. It will be seen that the 33-foot length of new tubing lowered the observed heating value, during the first few minutes, by about 2 per cent. After 29 hours the observed heating value of the gas was still about 0.5 per cent lower than when passed through the old tubing. The effect was not due to leakage in the ordinary sense; i. e., when the gas was shut off at the burner, observation of the meter indicated that there was no appreciable leakage. The precaution to be observed to eliminate this source of error is to use tubing thoroughly saturated with the gas, and as only 4 or 5 feet of tubing, or much less in a permanent installation, are necessary,

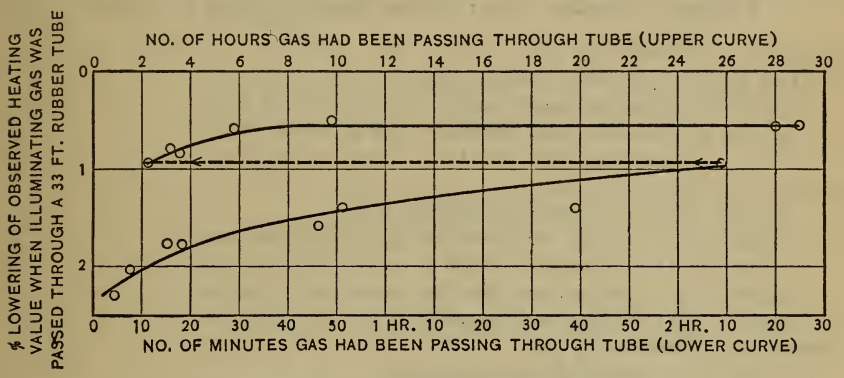


Fig. 19.—*Effect of new rubber tubing on heating value*

the effect will be negligible after the tubing has been in contact with the gas for several hours.

15. EFFECT OF COOLING GAS ON HEATING VALUE AND ON CANDLEPOWER

Alternate tests were made of the heating value of illuminating gas as drawn directly from the holder and as drawn through a copper coil immersed in melting ice. The decrease in the observed heating value due to lowering the temperature (for a brief interval) to nearly 32° F was 0.7 per cent. Similar experiments on the candlepower showed a decrease in candlepower of nearly 12 per cent. These experiments were made in the early autumn so that the gas had not been previously exposed to low temperatures in the mains. That the effect of exposure of oil-enriched illuminating

gases to low temperatures results in a far greater change in their candlepowers than in their heating values is so well known that further experiments along this line seemed unnecessary for the purposes of this investigation, the important point being merely to draw attention to the occurrence of such changes.

16. DETERIORATION IN HEATING VALUE OF GAS IN HOLDER

The data summarized in Table 24 show that the illuminating gas used in these experiments deteriorated in heating value when allowed to stand in contact with water in the 5 cubic foot holder.

TABLE 24

Change in Heating Value of Gas During Storage in Holder

Sample No. 1, illuminating gas:
July 30, 1913, gas holder filled at 9.30 a. m.
July 30, 1913, heating value found at 11.30 a. m.=660 Btu.
July 30, 1913, heating value found at 3.45 p. m.=661 Btu.
July 31, 1913, heating value found at 4.15 p. m.=653 Btu.
Sample No. 2, illuminating gas:
August 1, 1913, gas holder filled at 10.36 a. m.
August 1, 1913, heating value found at 10.45 a. m.=661 Btu.
August 1, 1913, heating value found at 4.00 p. m.=661 Btu.
August 2, 1913, heating value found at 1.00 p. m.=657 Btu.
August 4, 1913, heating value found at 11.00 a. m.=648 Btu.
Sample No. 3, illuminating gas:
August 4, 1913, gas holder filled at 2 p. m.
August 7, 1913, heating value found at 10.30 a. m.=658 Btu.
August 7, 1913, heating value found at 4.00 p. m.=659 Btu.
August 8, 1913, heating value found at 9.30 a. m.=654 Btu.

It will be seen that the deterioration amounted to 2 per cent in the course of several days. The magnitude of this effect would probably be different for gases of very different composition. It might also be expected that the rate of change might be different with a holder in which the area in contact with the water was different. It is therefore evident that if the object in view is the determination of the heating value of the sample of gas when drawn from the mains, the sample should be tested shortly after the gas holder is filled, or if the gas is stored for some time before testing, the effect of storage under the prevailing conditions should be investigated.

17. RÉSUMÉ OF FACTORS AFFECTING HEATING VALUE DETERMINATIONS

The foregoing discussion of the errors that may affect the various measurements and manipulations incident to the determination of heating values with flow calorimeters may, at first sight, seem rather formidable and leave the impression that the final accuracy of such determinations may not be as high as is desirable or even as is required in industrial testing. However, experience has shown that, if due attention is given to the precautions that have been shown to be of importance, an accuracy better than 0.5 per cent is attainable, and in ordinary routine testing an experienced observer should obtain results accurate to within about 1 per cent.

Thus it has been shown:

1. There is little probability of error due to incomplete combustion if the calorimeter is not operated at too high a rate of gas consumption.

2. Care is necessary in measuring the rise of temperature of the water; standardized thermometers should be used and the thermometer corrections and stem corrections should be applied.

3. If the calorimeter is operated with the inlet water at room temperature, if the burner is provided with radiation shields and is properly mounted within the calorimeter, if the calorimeter is operated at the normal rate and the correction for effect of atmospheric humidity is applied, the remaining heat losses will, for most calorimeters, introduce no significant error, while, if such losses are significant for the calorimeter used, a correction may be applied.

4. If the inlet water is not at room temperature the corrections necessary on this account may be readily applied.

5. The flow of water and of gas can readily be made sufficiently constant.

6. By waiting until the calorimeter is in thermal equilibrium (from 5 to 30 minutes, depending on the calorimeter used) no significant error due to its lag will be introduced unless there are considerable variations in the heating value of the gas being tested, in the rate of flow of gas or water, etc.

7. With a properly designed calorimeter, the drainage from which is uniform, the measurement of the condensed water offers no difficulty.

8. Care is necessary in manipulating the change-over device, since large accidental errors may be introduced in this operation, although no significant constant error need be introduced.

9. The weighing or measuring of the water with sufficient accuracy presents no difficulties.

10. Great care must be exercised in calibrating the gas meter and in making the necessary adjustments in its subsequent use. The other operations incidental to the measurement of gas volumes need introduce no significant error.

11. If tests are made regularly for leakage of gas, the effects of leakage may easily be reduced to negligible proportions.

12. With a standardized mercury barometer, the accuracy required in gas testing is easily attainable.

13–16. Errors may be introduced on account of changes in the character of the gas, due to various influences, the effect of which, however, may be easily avoided.

It appears therefore that the accuracy attainable in heating value determinations with flow calorimeters is mainly limited by errors in adjusting the gas meter, in measuring the temperature rise of the water, and in manipulating the change-over device, since the errors due to other factors may, by proper procedure, be made nearly, if not quite, negligible.

VIII. COMPARISON OF HEATING VALUES OF GASES DETERMINED WITH FLOW CALORIMETERS WITH THOSE OBTAINED WITH CALORIMETERS OF THE BERTHELOT BOMB TYPE

1. APPARATUS AND METHODS

In order to obtain a check on the accuracy of determinations of the total heats of combustion of gases, as made with industrial flow calorimeters, several gases having quite different heating values, viz, a natural gas, an oil enriched illuminating gas and nearly pure hydrogen were burned in a Junkers and in a Hinman-Junkers calorimeter of the flow type, and in a Williams and in a Kroeker-Peters calorimeter of the Berthelot bomb type. In

calorimeters of the bomb type the combustion takes place at constant volume. A suitable correction was therefore applied (dependent upon the change of volume occurring in combustion at constant pressure) to reduce the results obtained with the bombs to the corresponding values at constant pressure. The Williams bomb was provided with a gold lining; the Kroeker-Peters bomb with an enamel lining. The bombs were used in a specially designed calorimeter in an inclosure surrounded on all sides by a constant temperature water jacket. The temperature changes of the calorimeter were measured by means of a calorimetric platinum resistance thermometer and a special Wheatstone resistance bridge capable of measuring small temperature changes to one or two ten-thousandths of a degree. The entire calorimetric equipment has been in use at the laboratories of the Bureau for several years in an extended series of researches and full details will be published in subsequent communications.

The internal volumes of the bombs were determined in the following manner: The bomb, immersed in a water bath at known temperature, was nearly filled with freshly boiled distilled water; the bomb was then exhausted by a motor driven Geryk pump and the water thus boiled at reduced pressure to expel all traces of air remaining in the bomb; distilled water was then run into the bomb to completely fill it. From the mass of water required to completely fill the bomb, the volumes of the Williams and of the Kroeker-Peters bombs were found to be 606.1 cc and 266.6 cc, respectively, at 28° C.

The bomb, containing 0.5 cc of water, was connected by means of a three-way stopcock, alternately to a vacuum system, in which the pressure was about 0.1 atmosphere, and to the supply of gas, the heat of combustion of which was to be determined. The gas was drawn from the gas holder, at a pressure of a few inches of water above atmospheric, and was in equilibrium with water, so that the gas was practically saturated with water vapor at room temperature.

To insure that the gas in the bomb was saturated with water vapor at the known temperature of the bath, the bomb, after being alternately evacuated and filled with the gas a number of times, was immersed for some minutes in a water bath the tem-

perature (usually about 100°–110° F) of which was considerably above that of the room, was again evacuated and again connected to the gas supply. This precaution was really unnecessary, as was shown by the results of a number of experiments in which it was omitted. The bomb was then transferred to a thermostatic water bath at room temperature and after taking up the temperature of this bath, was momentarily opened to the air, through the three-way stopcock, which in the meantime had been disconnected from the vacuum system. The valve of the bomb was then closed. Diffusion of air into the bomb, while it was open to the atmosphere, was prevented by the fact that the connection between the interior of the bomb and the atmosphere was through a narrow tube filled with the same gas as that contained in the bomb. The volume of saturated gas contained in the bomb was equal to the volume of the bomb as determined above, the pressure of the gas being equal to the atmospheric pressure at the instant the valve was closed, and the temperature being that of the water bath in which the bomb was immersed.

Oxygen (95+ per cent, with the residue mainly argon), in excess of that required for complete combustion of the contained gas, was then run into the bomb, the amount being calculated from the indications of a calibrated closed end mercury manometer connected to the oxygen supply piping.

The bomb was then placed in the calorimeter, and after a suitable series of temperature observations to obtain the rate of rise of temperature during the preperiod, the mixture of gas and oxygen was fired, at a given time, by heating momentarily to incandescence a short length (a few mm) of 0.05 mm platinum wire between the electrodes within the bomb, by means of current from a 2-volt storage cell in series with a suitable resistance. The energy thus supplied by the firing current was absolutely negligible. Temperature observations were then continued during the so-called middle and after periods, from which observations was deduced the temperature rise, corrected for gain or loss of heat from the surroundings. The water equivalents of the calorimeters (including bomb, can, stirrer, thermometer, and water) had been carefully determined in previous investigations by a method of elec-

trical standardization. These data were again checked by H. G. Barrott by burning in the calorimeter standard combustion samples of benzoic acid; the agreement between the water equivalent thus determined and the older data was of the order of 1 part in 1000.

After the conclusion of each gas combustion, the interior of the bomb was washed with distilled water and the washings were titrated with a one-tenth normal solution of NaOH. As the oxygen used contained but a trace of nitrogen, the correction thus determined for the nitric acid formed in the combustion, and for any sulphuric acid resulting from traces of sulphur in the gas, was so small that it could have been entirely neglected, never exceeding 1 part in 1200 of the heat involved in the combustion.

2. COMPARISONS WITH NATURAL GAS

The results of determinations of the heating value of a sample of natural gas from the fields near Independence, Kans., as carried out with the Junkers and with the Hinman-Junkers flow calorimeters and with the Williams and with the Kroeker-Peters bombs are summarized in Table 25. The gas had been filled into a 5 cubic-foot steel cylinder from the discharge line of a compressor at a pressure of 250 pounds per square inch. For this sample of natural gas the Bureau is indebted to Messrs. A. B. Macbeth and J. B. Klumpp.

As will be seen from Table 25, the experimental conditions for the tests with the flow calorimeters were varied in many ways to obtain a check on the reliability of the results. Different calorimeters were used; the rate of gas consumption was varied; inlet and outlet water thermometers were interchanged and different pairs of thermometers were used; different wet meters were used, which were repeatedly calibrated, often both before and after the tests; by varying the air supply the character of the flame was changed from a partly luminous to a strongly oxidizing flame; different Bunsen burners were used, one with several different size tips (2.2, 1.6, 1.1 mm) substituted for the usual 2.2-mm tips used with illuminating gas, and a Méker burner with a 1-mm tip, to give the characteristic Méker flame; the pressure of the gas both

in the meter and at the burner tip was varied, and the gas was burned at different rates. During the experiments the atmospheric humidity varied between 40 per cent and 80 per cent and the temperature between 75° F and 85° F.

TABLE 25

Determinations of Heating Values of a Sample of Natural Gas from Fields near Independence, Kans.

DATA OBTAINED WITH FLOW CALORIMETERS

Date	Series Nos	Humidity	Room temperature	Gas rate	Observed heating value	Net heating value	Total heating value	Remarks
1913		Per cent	°F	Cu. ft. hr.	Btu	Btu	Btu	
June 17	1	49	84	4.0	989	903	997	
18	2	43	82	4.0	990	904	999	
19	4	56	82	4.0	991	903	997	
20	5	62	82	4.0	993	904	998	
20	6	62	82	2.7	989	903	(998)	Total calc. from net.
20	7	62	82	4.7	994	904	(999)	Do.
20	8	62	82	4.0	993	902	998	
23	9	64	80	4.0	996	903	999	
23	11	70	77	4.0	996	904	999	
24	12	71	77	4.0	992	900	995	
25	13	74	80	4.0	996	902	999	Another gas meter in remaining tests.
25	14	78	80	4.0	996	902	998	Excess air in Bunsen.
25	15	78	80	4.0	(987)	.....	.....	Incomplete combustion shown by odor of products.
25	16	78	80	4.0	998	904	999	
26	17	72	80	4.0	994	902	996	Meker burner.
26	18	72	80	4.0	997	903	999	
26	19	73	81	6.5	997	903	999	Damper open.
26	20	78	81	3.0	997	.....	999	Hinman - Junkers Calorimeter No. 164; normal rate.
28	21	53	87	4.0	991	902	999	
28	22	58	86	4.0	992	903	998	Very large excess of air in Bunsen.
July 14	23	49	84	4.0	991	902	1000	
16	25	40	82	4.0	988	902	997	
Mean						903	998	

TABLE 25—Continued

DATA OBTAINED WITH THE WILLIAMS AND THE KROEKER-PETERS BOMB CALORIMETERS

Date	Series No.	Excess oxygen	Liters of saturated gas burned, measured at 28° C, 760 mm	Corrected temperature rise of calorimeter	Heat capacity of calorimeter	Correction for HNO_3 formed	Heat of combustion at constant volume, per liter of saturated gas, measured at 28° C, 760 mm	Heat of combustion at constant pressure, per liter of saturated gas, measured at 28° C, 760 mm
1913		Per cent		°C	15° cal.	calories	calories	calories
June 18	3	13	0.6042	1.6529	3035	−2.1	8299	8347
18	3	16	.6034	1.6497	3035	−1.8	8295	8343
18	3	34	.6033	1.6487	3035	−2.7	8290	8338
18	3	26	.6031	1.6469	3035	−2.7	8283	8331
23	10	16	.6044	1.6537	3035	−2.4	8300	8348
23	10	18	.6037	1.6486	3035	−2.4	8285	8333
July 15	24	20	.2638	0.6415	3410	− .4	8291	8339
15	24	20	.2637	.6415	3410	− .4	8294	8342
15	24	30	.2635	.6405	3410	− .5	8287	8335
Heat of combustion of 1 liter saturated gas, measured at 28° C, 760 mm =							8291	8339
∴ Total heating value = 1001 Btu per cubic foot								

Each series in Table 25 consisted of from two to four separate determinations. The pressure of the gas in the cylinder at beginning of the series of experiments was 260 pounds per square inch, and this was reduced to 40 pounds per square inch at the end of the experiments.

The results obtained under all these varied conditions were quite consistent. The mean total heating value of the sample of natural gas contained in the cylinder, as determined with the flow calorimeters, was found to be 998 Btu per cubic foot.

The mean total heating value of the same sample of gas, as determined by the bomb calorimeters, was 1001 Btu per cubic foot. The difference between the results found with the two methods of calorimetry is within the limits of the combined effects of experimental errors.

3. COMPARISONS WITH HYDROGEN

Nearly pure hydrogen was burned in the Junkers calorimeter No. 1209 and in the Williams bomb calorimeter. The hydrogen was produced electrolytically from a solution of caustic potash and was collected over water in the 5-cubic-foot gas holder. While the hydrogen was probably of a fair degree of purity, the holder and connections having been washed out several times before the final filling, no attempt was made to purify the gas delivered by the generator, and no analyses of the gas were made, the object in view being not a determination of the heating value of hydrogen but a comparison of results obtained with flow and with bomb calorimeters, respectively, when applied to a gas of low heating value.

A preliminary calculation showed that if the Junkers calorimeter were used with the usual damper furnished with it (two 15-mm openings) the normal rate for hydrogen would be too large to permit of accurate metering. A damper having two 8-mm openings was therefore substituted, and with this damper the normal rate for hydrogen was found to be about 7.3 cubic feet per hour.

The manipulation of the bomb was similar to that in the experiments with natural gas.

The results obtained for the heat of combustion of the nearly pure hydrogen with the Junkers calorimeter and with the Williams bomb calorimeter, together with the more important data relating to these experiments, are summarized in Table 26.

TABLE 26

Determination of Heating Value of a Sample of Nearly Pure Hydrogen

DATA OBTAINED WITH JUNKERS CALORIMETER NO. 1209

Date	Experiment No.	Humidity	Room temperature	Gas rate	Observed heating value	Net heating value	Total heating value
1913		Per cent	°F	Cu ft per hr	Btu	Btu	Btu
Aug. 12	1	55	77	7.3	318.5	269.6	318.6
12	2	55	77	7.3	318.4		318.5
15	6	59	78	7.3	317.4	269.2	317.9
15	7	59	78	7.3	317.5		318.0
Mean						269.4	318.2

TABLE 26—Continued

DATA OBTAINED WITH WILLIAMS BOMB CALORIMETER

Date	Experiment No.	Excess o oxygen	Liters of saturated gas burned, measured at 28° C, 760 mm	Corrected temperature rise of calorimeter	Heat capacity of calorimeter	Correction for HNO_3 formed	Heat of combustion at constant volume, per liter of saturated gas, measured at 28° C, 760 mm	Heat of combustion at constant pressure, per liter of saturated gas, measured at 28° C, 760 mm
1913		Per cent		°C	15° calories	calories	calories	calories
Aug. 14	3	50	0.6005	0.5166	3035	−1.7	2608	2644
14	4	90	.6006	.5174	3035	−1.8	2612	2648
14	5	130	.6005	.5181	3035	−2.5	2614	2650
Heat of combustion of 1 liter saturated gas, measured at 28° C, 760 mm=							.....	2647
∴ Total heating value=317.6 Btu per cubic foot								

4. COMPARISONS WITH ILLUMINATING GAS

With gases like hydrogen or like natural gas, which are quite stable in character, the results found for the total heating value by the flow calorimeter method were in excellent agreement with the results found by the calorimetric bomb method. The results obtained, however, in comparing these methods when an oil-enriched illuminating gas was used were not satisfactory. A number of tests by the two methods were made which seemed to show that the heating values determined with the bomb were nearly 1 per cent lower than the values found with the Junkers calorimeter. The earlier tests were not all made on the same day, however, and as it had developed from these experiments that the gas standing in the holder in contact with water suffered a progressive deterioration in heating value (see p. 98), another series of tests by the two methods was planned which was completed in one day, the determinations with the two bombs already described being preceded and followed by determinations with the Junkers calorimeter. The details of manipulation were similar to those previously described in connection with the experiments on natural gas. The excess of oxygen in the bombs, over that required for combustion, was varied from 25 per cent to 100 per cent. The heat of combustion obtained with the bombs was again about 1 per cent lower than that found with the flow calorimeter.

This apparent difference in the results found by the two methods is, so far as the evidence at hand shows, not a real one due to the instruments, but is to be attributed to the character of the gas, since when the more stable and homogeneous gases were used no such difference between the results obtained with the two methods was found to exist.

The difference in the results found with the Junkers flow calorimeter and with the bomb calorimeters was attributed to some change in the character of the unstable illuminating gas when allowed to expand into the evacuated bomb. Accordingly, it was decided to fill the bomb by drawing gas through it for some time, i. e., by a method of transpiration instead of by the method of successive evacuations previously used. This method could not, however, be used with the Williams bomb, which had only one inlet. To eliminate the possible effect of selective absorption of the constituents of the gas by the rubber tubing, the latter was replaced by glass tubing. Under these conditions the Kroeker-Peters bomb gave results for illuminating gas about 0.5 per cent higher than were found with the Junkers flow calorimeter.

In view of the marked differences found for the illuminating gas, when used under different conditions in the bomb calorimeter, it was decided to substitute for the unstable illuminating gas a mixed gas of more stable character and having a heating value approximately equal to that of the illuminating gas. This mixed gas was produced in the gas holder by mixing natural gas with hydrogen, produced electrolytically. One set of results found with this mixed gas is summarized below.

It will be seen that the results obtained with the several calorimeters are in satisfactory agreement.

It is not yet clear why the illuminating gas, when filled into the Kroeker-Peters bomb by the method of transpiration, should give results about 0.5 per cent higher than those found with the Junkers calorimeter. In this connection it should be remarked that the Kroeker-Peters bomb gave results a few tenths of a per cent higher than the Williams bomb. The difference may be due to the presence of the enamel lining. Thus, for example, no acidity is detected in the washings of this bomb after a combustion. The

platinum-lined Kroeker-Peters bomb was not used for the reason that the explosion of the gas would be likely to tear loose the platinum lining. If this difference between the two bombs is a real one, the discrepancy above referred to for illuminating gas practically disappears. At any rate the small outstanding discrepancy for the illuminating gas is evidently a problem in bomb calorimetry requiring further investigation and it was not deemed worth while withholding the results of the present investigation awaiting the solution of that problem.

TABLE 27

Heating Value Determinations of Mixed Gas (Natural Gas and Hydrogen) with Junkers Calorimeter No. 1209 and with the Williams Gold-lined Bomb Calorimeter and the Kroeker-Peters Enamel-lined Bomb Calorimeter

Date	Expt. No.	Calorimeter.		
		Junkers	Williams	Kroeker-Peters
July 28, 1914	1	636		
	2	...	[a] 637	
	3	...	....	[a] 637
	4	...	[a] 636	
	5	...	....	[a] 639
July 29, 1914	6	...	[a] 635	
	7	...	....	[a] 639
	8	...	[a] 635	
	9	...	....	[b] 639
	10	...	....	[b] 638
	11	636		
Mean	.....	636	636	638

[a] Bomb filled with gas by method of successive evacuation and refilling.
[b] Bomb filled by drawing gas through for long time.

From the agreement of the results found with the Junkers calorimeter and the bomb calorimeters when used with natural gas, with hydrogen, and with the mixed gas it seems safe to conclude that the heating values found by the above two very different methods of calorimetry are in agreement to within the limits of accuracy of the work (a few tenths of 1 per cent).

IX. TESTS OF VARIOUS GAS CALORIMETERS

In this section are summarized the results of such special tests as were made on the several calorimeters listed in Table 1. Many special experiments relating to these calorimeters, and which illustrate the general principles underlying the operation of flow calorimeters, have been described in previous sections of this paper.

The essential details of construction and the principle of action (briefly discussed on p. 17) of the various calorimeters will be readily understood by examination of the photographic reproductions and the sectional drawings of the instruments. Detailed explanations relating thereto, which may be found in trade catalogues and in published papers, have therefore been omitted or reduced to a minimum.

Criticisms have been made here and there which often relate to minor defects of design or construction that are very easily remedied. Such criticisms are in no sense a condemnation of the instrument and they have been made mainly with the object of calling the attention of the user to such defects, so that he may be on the lookout for them. Such minor defects are particularly likely to occur where types have not been standardized as to details of manufacture.

As the Junkers calorimeter No. 1209 had been compared with calorimeters of the Berthelot bomb type, and furthermore, as an exhaustive investigation had been made of the various constants of and heat losses from this calorimeter, it was used to determine the total and net heating values of various samples of gas, simultaneous determinations being made on the same samples of gas with the calorimeter under investigation. The same meter was used throughout such a series of experiments, so that the errors incident to metering were, to a large extent, eliminated from the results.

1. JUNKERS CALORIMETER (ORIGINAL TYPE)

Description.—This calorimeter is illustrated in Figs. 20 and 21. The water from the source of supply enters the inlet overflow wier, passes downward through the tube on the left, through a valve for controlling the rate of flow, past the bulb of the inlet-

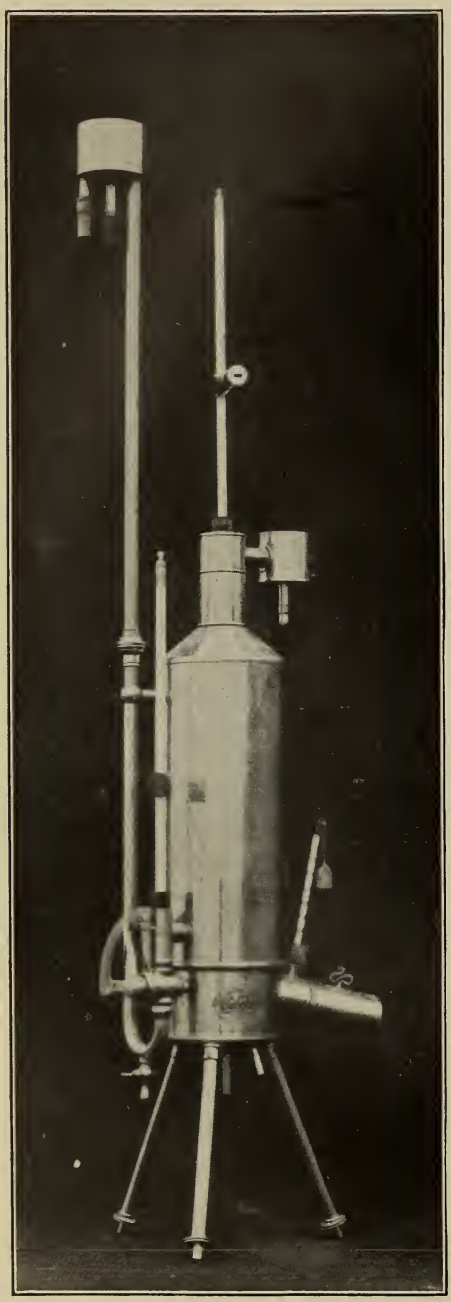


Fig. 20

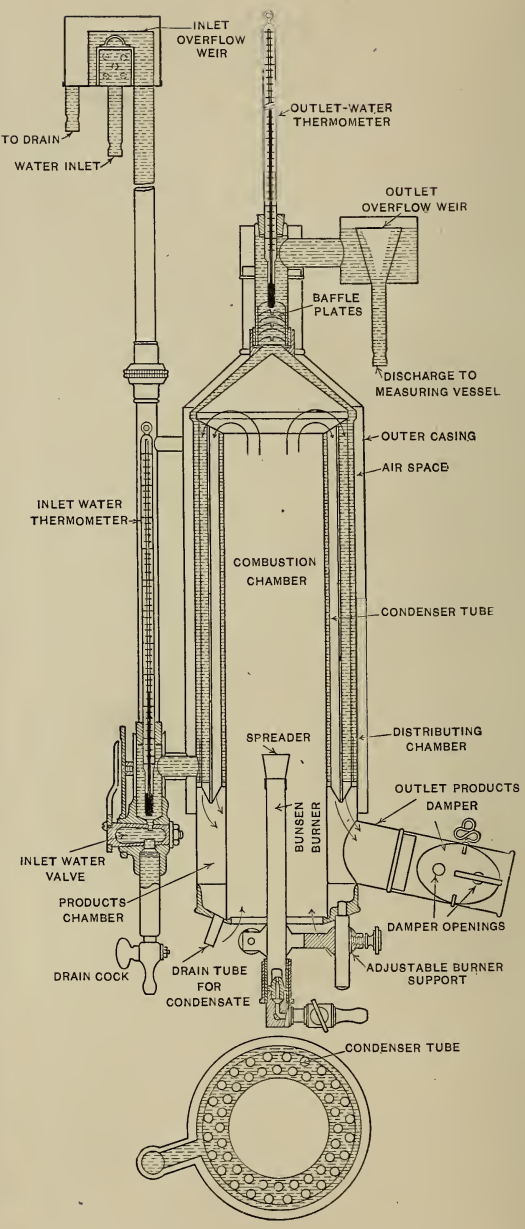


Fig. 21

Junkers calorimeter (original type)

water thermometer and enters a distributing chamber at the bottom of the calorimeter. The water then flows upward over the outside of a set of vertical condenser tubes in the inner annular cylindrical space surrounding the combustion chamber, through the conical space above the combustion chamber and through the small cylindrical space at the top, in which are placed several mixing diaphragms to thoroughly mix the stream of water before it reaches the bulb of the outlet-water thermometer, in order that the latter will assume the true mean temperature of the effluent stream of water, which has taken up the heat from the products of combustion. The water then passes out of the calorimeter, through the short horizontal tube at the top, into the outlet overflow wier, from which it is discharged. The total water content of this calorimeter is somewhat in excess of three pounds.

The gas is burned in a Bunsen burner within the combustion chamber. The products of combustion pass upward to the top of the combustion chamber, then downward through the condenser tubes mentioned above, into the products chamber at the bottom of the calorimeter, and thence are discharged into the air through an outlet tube in which is placed the bulb of the products thermometer and also an adjustable damper. The entire calorimeter, with the exception of the products chamber at the bottom, is inclosed in a concentric nickel-plated casing of thin copper, thus forming an air space between the casing and the calorimeter proper. A small hole at the bottom of the casing permits the escape of any water which may leak into the air space, and thus provides a means of indicating the presence of leaks in those parts of the calorimeter which are inclosed by the outer casing.

The design of this calorimeter has been criticized on account of the inconvenience in reading the inlet- and outlet-water thermometers, which are at different levels. When the inlet water is maintained at constant temperature, so that this temperature has to be read only at the beginning and end of a test, the inconvenience referred to is of little importance. In some of the modifications of this calorimeter to be discussed later, the thermometers are brought to the same level by mounting the inlet-water thermometer in the inlet water pipe, at a greater distance from the

bottom of the calorimeter. However, in the modified calorimeters, the inlet-water thermometer, as well as the inlet water valve in some models, are in the descending stream of water, instead of in the ascending stream, as in the original model, thus increasing the possibility of the formation of air traps, with consequent irregularity in the rate of water flow.

Special Tests.—It was shown on p. 57 that when the burner holder was modified so that the burner could be raised sufficiently to bring the base of the flame about 1.5 inches above the horizontal plane defined by the boundary surface between the bottom of the water chamber and the top of the products chamber at the base of the calorimeter and when radiation shields were used on the burner, reheating of the products in this lower chamber was prevented, so that the products then escaped from the calorimeter at practically the temperature of the inlet water. It was also shown that the use of radiation shields on the burner raised the observed heating value several tenths of 1 per cent.

The combustion chamber is of ample size and the spaces provided for the passage of the products of combustion are of sufficient size to permit of burning illuminating gas at rates up to 15 cubic feet per hour. Experiments made to determine the volume of entering air and of discharged products, for various rates of gas consumption, have been described on p. 64. The damper furnished with the instrument had two 15-mm openings and with this damper closed, the normal rate of gas consumption (defined on p. 69) was about 7 cubic feet per hour for illuminating gas (650 Btu) and about 4 cubic feet per hour for natural gas (1000 Btu).

The calorimeter is so designed and constructed that the drainage therefrom, of the water resulting from the condensation of aqueous vapor from the products of combustion, is regular, so that net heating values can be accurately determined.

The efficiency of the calorimeter as a heat absorber, defined in a somewhat restricted sense as the ratio of the amount of heat absorbed by the water flowing through the calorimeter (product of mass of water, its specific heat and its indicated rise in temperature) to the amount of heat supplied as electric energy to an electric heating coil in the combustion chamber, has been con-

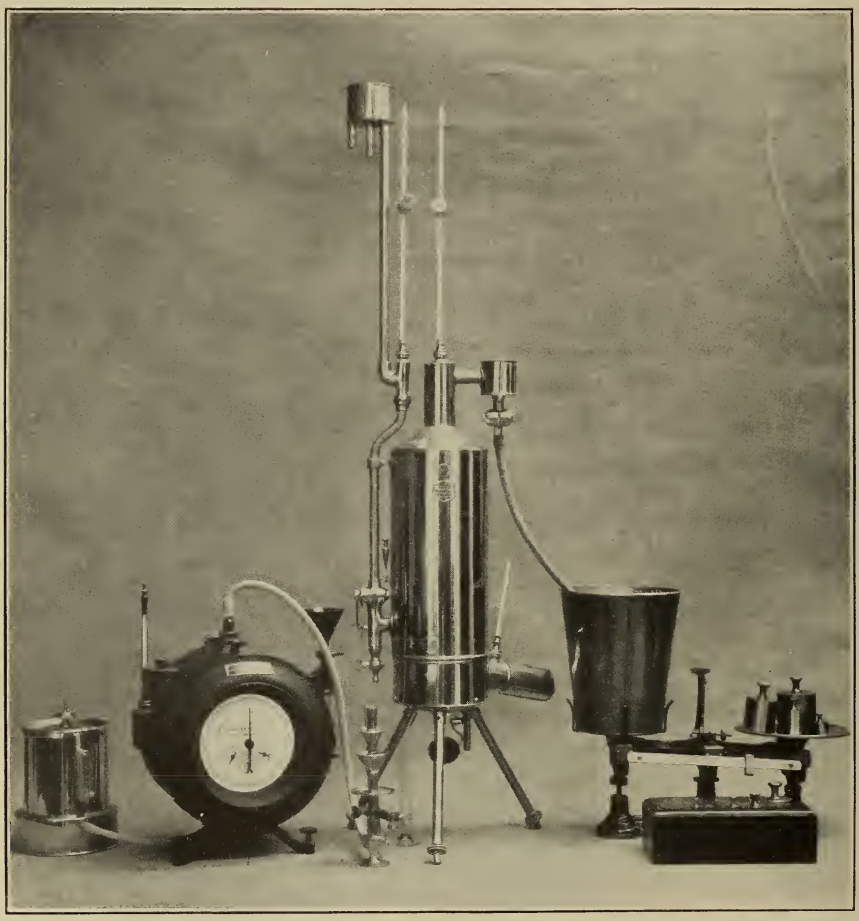


Fig. 22.—*Hinman-Junkers calorimeter*

sidered on p. 50, where it was shown that the value of this ratio, for this calorimeter, was above 0.996.

Comparisons with Bomb Calorimeters.—The determinations of the total heating values of a sample of natural gas and of nearly pure hydrogen, the experimental data for which are given on p. 104 and p. 106, have shown that total heating values as determined with the Junkers calorimeter No. 1209, were in agreement with the heating values found with calorimeters of the Berthelot bomb type, to within the limits of experimental errors of the measurements (viz, about 0.3 per cent).

2. HINMAN-JUNKERS CALORIMETER

Description.—This calorimeter, illustrated in Fig. 22, is a close copy of the Junkers calorimeter described in the preceding section. Modifications have been made in a few minor details. The inlet and outlet water thermometers are mounted on the same level, both the inlet-water thermometer and the valve controlling the rate of water flow being in the descending stream of water. A three-way stopcock has been provided for diverting the effluent water to drain or to weighing bucket. In the later models the combustion chamber and the condenser tubes form a unit which can be removed from the casing to permit of cleaning the outside surfaces of the tubes which are in contact with the water, a feature which is very desirable, as it permits not only the removal of deposits from the outer surface of the condenser tubes, but also makes all parts of the calorimeter conveniently accessible for repairs. Each thermometer is mounted in a metal holder provided with a flange held in position by a screw cap, a mounting which makes the thermometers more liable to breakage than the flexible rubber stopper mounting used with other calorimeters, although, if the thermometer[21a] stems were protected by metal tubes with front and back suitably cut away to permit of reading and to provide for proper illumination, this type of mounting would be very serviceable in use. This calorimeter also differs from the Junkers calorimeter in the dimensions of some of the parts. The total water content is somewhat in excess of 3 pounds.

[21a] This form of mounting for the thermometers has been adopted in later models.

A calorimeter of this type (No. 91) was kindly placed at the disposal of the Bureau by Mr. J. B. Klumpp.

Special Tests.—It was found that reheating of the products at the base of the calorimeter could be prevented if the burner were raised as described in the preceding section relating to the Junkers calorimeter. The use of radiation shields on the burner, either those furnished with the instrument or others made of thin disks of aluminum suitably perforated, resulted in increasing the observed heating values by about 0.7 per cent. Later experiments with another calorimeter of the same type indicated that this increase was somewhat less than 0.5 per cent.

The size of the combustion chamber and of the spaces provided for the passage of the products of combustion are approximately the same as in the Junkers calorimeter. The damper furnished with the calorimeter had two one-half inch openings, and with this damper closed the normal rate of gas consumption was about 5 cubic feet per hour for illuminating gas (650 Btu) and about 3 cubic feet per hour for natural gas (1000 Btu).

One of the calorimeters tested was defective in that only part of the water resulting from the condensation of aqueous vapor from the products of combustion was discharged through the spout provided for this purpose, while the remainder dripped from the lower edge of the wall of the combustion chamber.

The efficiency of the calorimeter as a heat absorber, determined from experiments with the electric heating coil, was found to be above 0.996.

Measurement of Total Heating Value.—Two Hinman-Junkers calorimeters (Nos. 91 and 164) were used to measure the total heating values of three samples of gas, two of illuminating gas and one of natural gas. The total heating values of these samples were determined as described on p. 110. The results of these determinations showed that if the observed heating values found with the Hinman-Junkers calorimeter were corrected for surface losses (which were practically the same as for the original type Junkers calorimeter), for effect of atmospheric humidity (by Tables 19 and 20), etc., the total heating values thus found were in agreement (0.2 per cent) to within the limits of experimental error with the total heating values that had been found for the gases used in the tests.

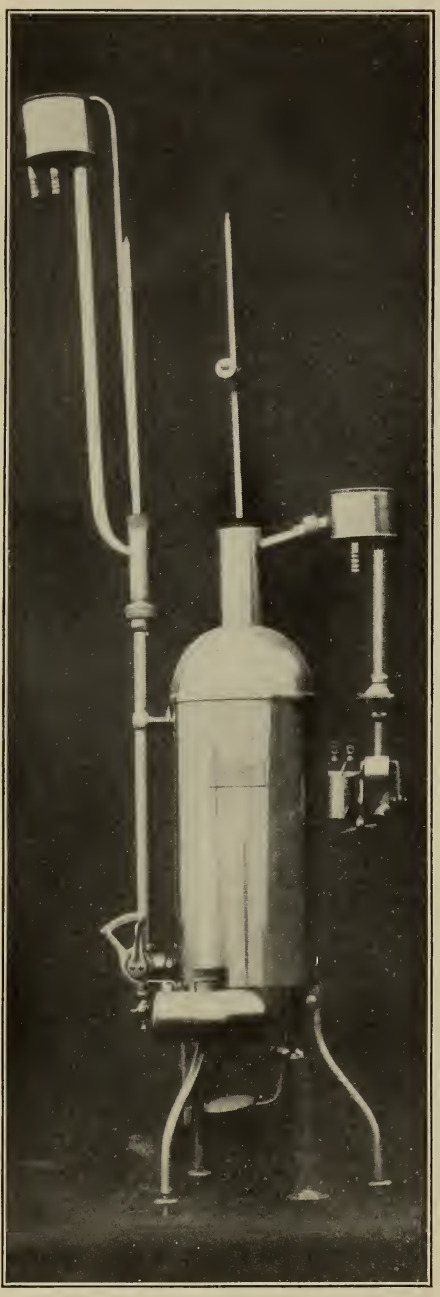


Fig. 23.—*Sargent calorimeter*

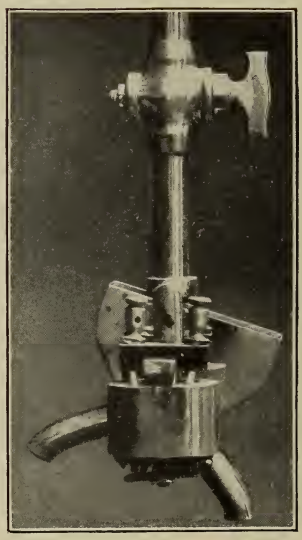


Fig. 23a.—*Enlarged view of automatic change-over device*

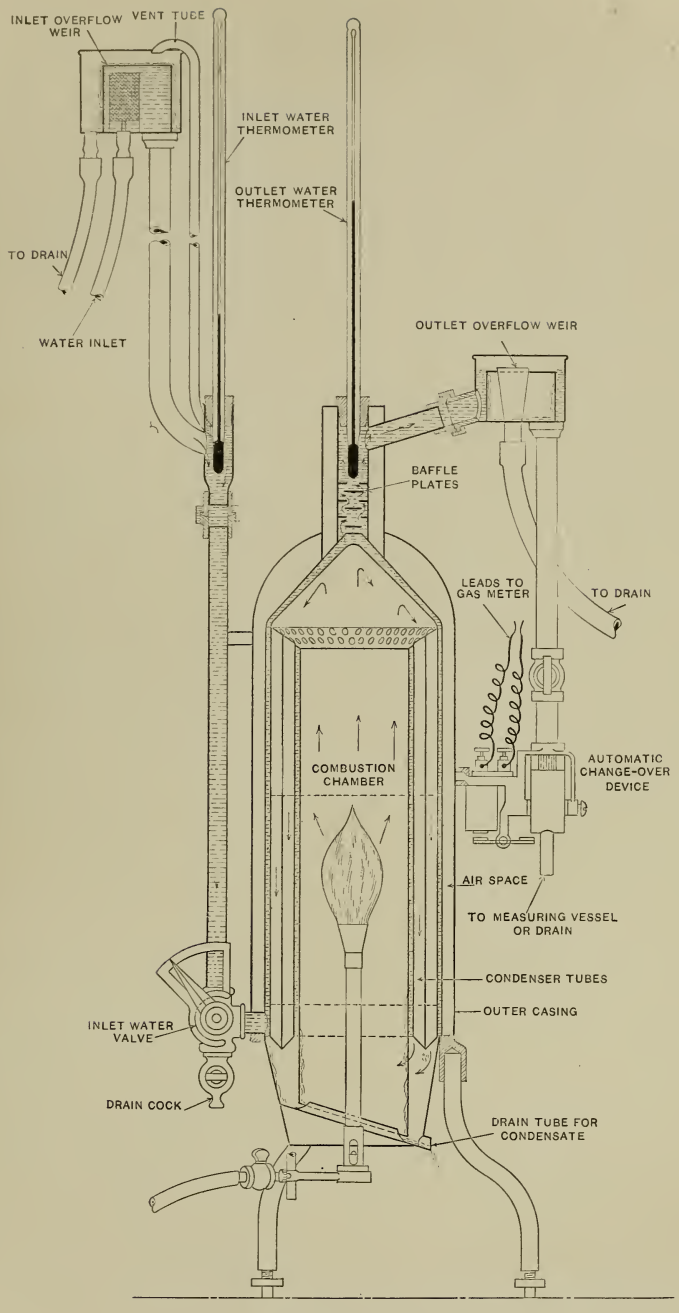


Fig. 24.—*Sargent calorimeter (section)*

3. SARGENT CALORIMETER

Description.—In the later models of this instrument the design of the Junkers calorimeter is followed very closely. In Figs. 23 and 24 are shown a photograph and a sectional drawing of one of these later models. A special feature is an automatic change-over device to divert the effluent stream of water from drain to weighing bucket, or vice versa. When the index of the meter passes through the zero position, it closes an electric circuit, thereby energizing an electromagnet which controls the operation of the change-over device. The inlet and outlet water thermometers are on the same level, and both the inlet-water thermometer and the valve controlling the rate of water flow are in the descending stream of water. A vent tube has been added for the purpose of permitting the escape of air which may accumulate around the bulb of the inlet-water thermometer. The total water content of this calorimeter is somewhat in excess of 3 pounds.

Special Tests.—The burner as furnished with the calorimeter could be set sufficiently high to avoid reheating of the combustion products in the products chamber at the base of the calorimeter, so that the products were discharged at practically the temperature of the inlet water. The radiation shields furnished with the burner, which were made of mica to permit observation of the flame in the calorimeter, gave the same result as perforated aluminum disk shields, the increase in the observed heating value due to the shields being of the order of 0.5 per cent.

The capacity of the spaces provided for the passage of the products of combustion is approximately the same as in the Junkers calorimeter. There were no openings in the dampers of the instruments tested. However, if the damper were made with two one-half inch openings, the normal rate of gas consumption, with damper closed, should be between 5 and 6 cubic feet per hour for illuminating gas. With the instrument as furnished, with no openings in the damper, the normal rate will depend upon the angular setting of the damper.

One of the calorimeters tested had to be modified to permit of the determination of net heating values, as part of the water

resulting from the condensation of aqueous vapor from the products of combustion collected in the outlet tube through which the products of combustion escaped.

The efficiency of one of the calorimeters as a heat absorber, determined from experiments with the electric heating coil, was found to be above 0.996.

Measurement of Total Heating Value.—Two Sargent calorimeters were used to measure the total heating values of several samples of illuminating gas. The total heating values of these samples were determined as described on p. 110. The results of these determinations showed that, if the observed heating values found with the Sargent calorimeters were corrected for surface losses (which were practically the same as for the original type Junkers calorimeter) for effect of atmospheric humidity (by Table 19), etc., the total heating values thus found were in agreement (0.2 per cent) to within the limits of experimental error with the total heating values that had been found for the gases used in the tests.

4. JUNKERS CALORIMETER (NEW TYPE)

Description.—This calorimeter, illustrated in Figs. 25 and 26, differs radically in design from the older type of Junkers calorimeter. The calorimeter is inclosed at the sides and top in a casing of thin sheet metal, nickel plated on the outside, the air space between the calorimeter proper and the outer casing being wide enough to accommodate the flattened tube through which the water from the inlet wier, after passing the bulb of the inlet-water thermometer at the top of the calorimeter, is led to the bottom of the calorimeter. The water then passes upward in an annular cylindrical shell, the inner wall of which forms the combustion chamber, outward at the top of this shell through four radial passages into the space above the combustion chamber, thence through a tube, in which is found the bulb of the outlet-water thermometer, to an overflow wier, from which it passes through a bent tube, which may be rotated in such a way as to divert the effluent stream from drain to graduate (or weighing bucket), or vice versa.

Both the inlet-water thermometer and the valve controlling the rate of water flow are in the descending stream of water. A

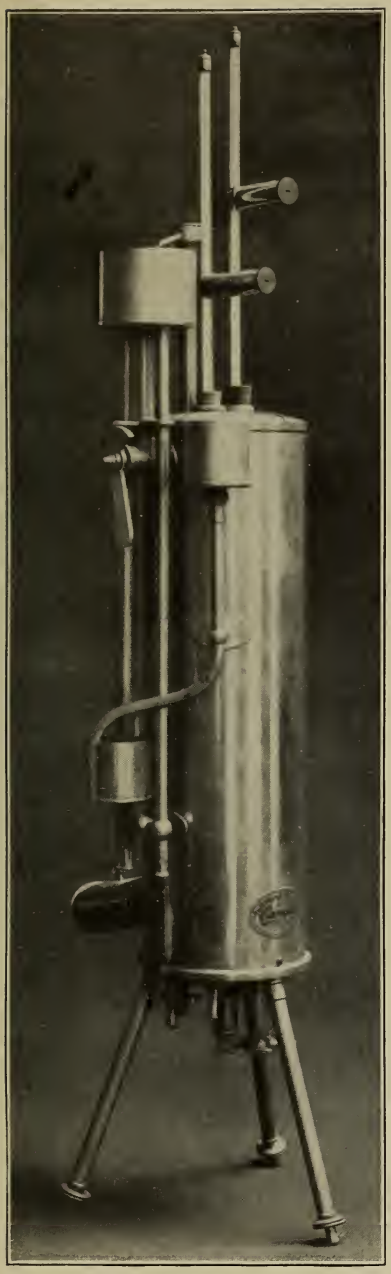


Fig. 25

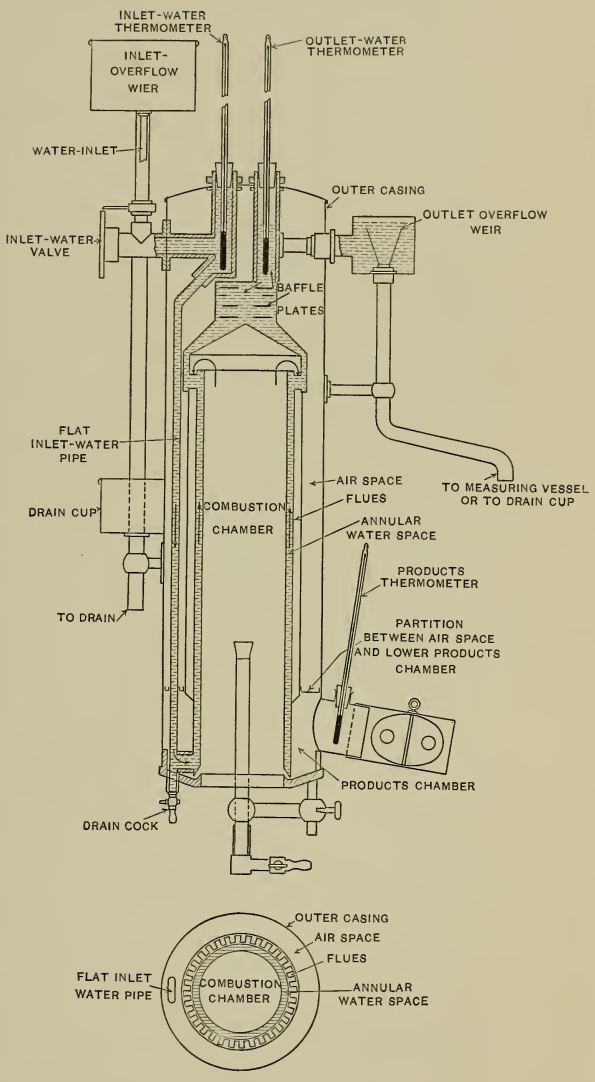


Fig. 26

Junkers calorimeter (new type)

vent tube has been added for the purpose of permitting the escape of air that may accumulate around the bulb of the inlet-water thermometer. The total water content of this calorimeter is about 1.5 pounds. The inlet and outlet water thermometers are mounted on the same level. For this and for other reasons calorimeters of the new type are somewhat more convenient of manipulation than those of the older type.

The heated products of combustion pass upward to the top of the combustion chamber, thence downward through the spaces shown in Fig. 26 (which are formed by bending sheet metal to the shape shown in the illustration) and thence into the products chamber at the bottom of the calorimeter, from which the products are discharged through the outlet-products tube.

The calorimeter tested, No. 1443, was kindly loaned for the purpose of this investigation by Mr. J. C. Dickerman, at that time chief gas tester of the city of Chicago.

Special Tests.—In this calorimeter the lower products chamber is separated from the combustion chamber by the annular shell of water, so that reheating of the products is avoided if the burner is set well within the combustion chamber. Owing to the fact that the spaces in which the products pass downward are not completely surrounded by the upward stream of water, the products of combustion escape at a temperature slightly (about 1° F) above that of the inlet water.

The effect on the observed heating values of the use of radiation shields was not determined for this calorimeter, as the order of magnitude of the effect of such shields was known from experiments with other calorimeters.

The flue capacity of this calorimeter is somewhat less than that of the older type of Junkers calorimeter. The normal rate of gas consumption for illuminating gas was about 5 cubic feet per hour with the damper (two 15-mm openings) closed, and about 7 cubic feet per hour with the damper open.

The calorimeter is so designed and constructed that the drainage of the water resulting from the condensation of aqueous vapor from the products of combustion is uniform, so that net heating values can be accurately determined.

Error in Indications of Outlet-Water Thermometer.—Early in the tests the fact developed that displacing the bulb of the outlet-water thermometer sidewise a short distance in the outlet water tube caused changes in the indications of the thermometer of as much as 0.3° F, corresponding, for an 18° rise in temperature, to about 1.7 per cent in heating value. Mr. Dickerman suggested that a mixing device be mounted in the outlet water tube ahead of the thermometer bulb. A mixing device, of the form shown in Fig. 27, was accordingly constructed and mounted in the outlet tube of the calorimeter. This mixer caused the water to flow through a central tube, in which were mounted a number of conical diaphragms, which changed the direction of flow as indicated by the arrows. After passing the thermometer bulb the water passed out of the top of this central tube and flowed downward in the annular space between this tube and the outlet tube and out through the side tube leading to the overflow wier.

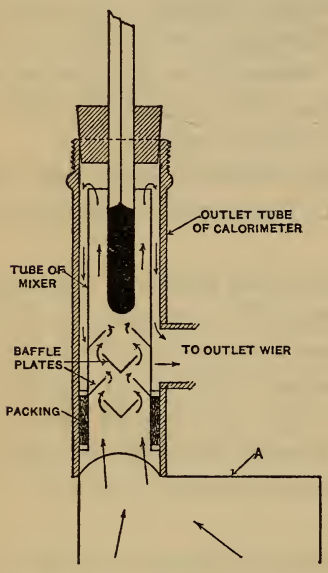


Fig. 27.—*Mixing device for outlet water in Junkers calorimeter (new type).*

With this mixer in position the thermometer apparently indicated the true mean temperature of the outlet water. It was found, however, that the readings of the outlet-water thermometer varied during the course of an experiment more than with the other calorimeters, probably on account of the accumulation of air bubbles under the nearly horizontal surface (A, Fig. 27), which caused a variation in the rate of flow of the water. That such was the case was indicated by the fact that shaking and tilting the calorimeter resulted in the visible liberation of air bubbles and in appreciable changes (over 1 per cent) in the rate of flow of water.

Determination of Total Heating Value.—The total heating value of a given sample of gas was determined as described on p. 110.

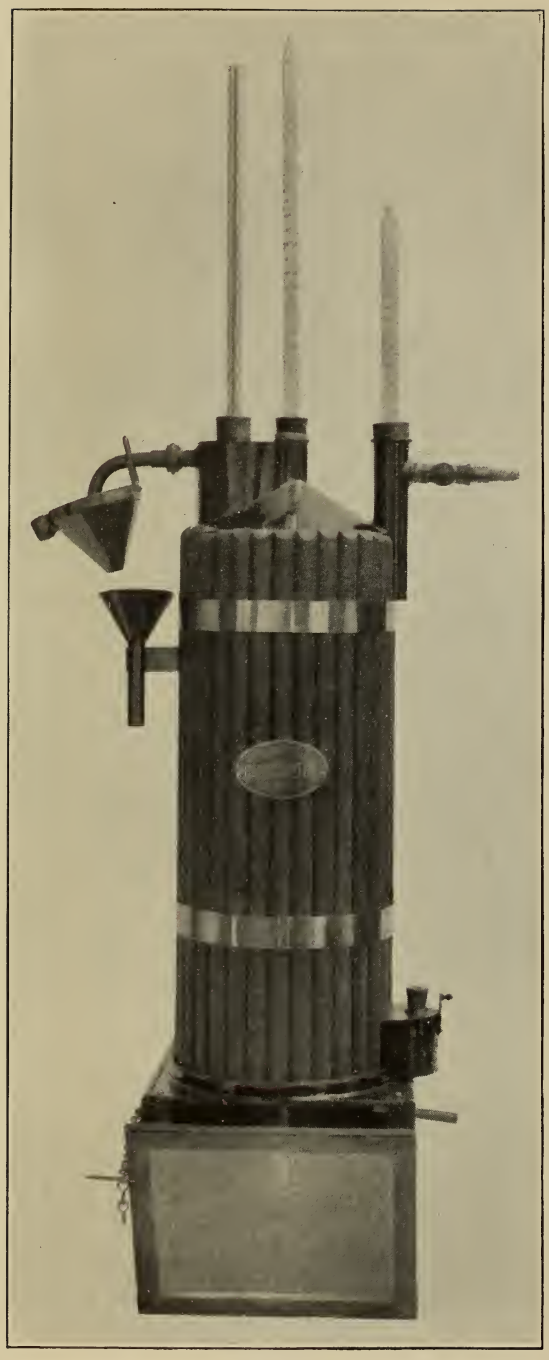


Fig. 28

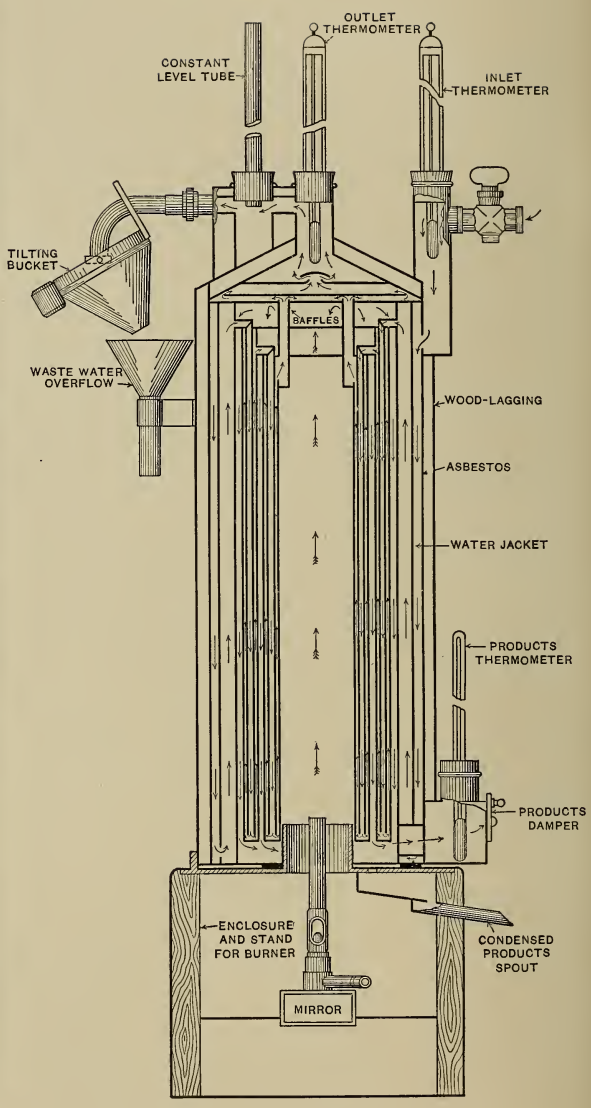


Fig. 29

Simmance-Abady calorimeter (English type)

Junkers calorimeter (new type) No. 1443, with the mixing device in the outlet-water tube and with radiation shields on the burner, was then used to measure the total heating value of the same gas. The results of a typical test are given in Table 28.

TABLE 28

Measurements of Total Heating Value with Junkers Calorimeter No. 1443 (New Type)

Calorimeter and method of operation	Total heating values
	Btu
Junkers No. 1209, operated at normal rate of 7 cubic feet per hour, damper closed	642
Junkers No. 1443, operated at normal rate of 5.1 cubic feet per hour, damper closed	641
Junkers No. 1443, operated at normal rate of 7.0 cubic feet per hour, damper open	641

The results show that, when the Junkers calorimeter No. 1443, new type, was provided with a suitable mixing device for the outlet water and with radiation shields on the burner, total heating values could be accurately determined.

5. SIMMANCE-ABADY CALORIMETER (ENGLISH TYPE)

Description.—This calorimeter, illustrated in Figs. 28 and 29, differs from the calorimeters already described in that the circulating water, instead of entering at the base of the calorimeter and passing upward and out at the top, enters a tube (in which is placed the bulb of the inlet-water thermometer) near the top of the calorimeter, passes downward in an annular space which is lagged on the outside with asbestos and wood and which forms the outer portion of the calorimeter, thence upward and downward in a series of concentric annular spaces, and finally out at the top of the calorimeter through a tube in which is placed the bulb of the outlet-water thermometer.

After passing the bulb of the outlet-water thermometer, the water enters a small space in which is supported a gauge glass and then is discharged from the calorimeter through a curved tube. A tilting bucket below this tube is provided to divert the water

from drain to graduate or vice versa. The total water content of calorimeters of this type is 12 to 14 pounds.

The inlet and outlet water thermometers are at the same level. No convenient means are provided for permitting the escape of air which may accumulate around the bulb of the inlet-water thermometer, so that it is desirable, before beginning a test, to loosen the stopper supporting this thermometer so as to permit the escape of the entrapped air.

The inner boundary of the last of the concentric annular spaces mentioned above forms the combustion chamber. The products of combustion pass upward to the top of the combustion chamber and thence downward, through one or the other of two annular spaces between the series of annular water spaces, to the base of the calorimeter, where they are discharged through an opening provided with an adjustable damper.

Special Tests.—The method of observation at one time recommended by the designers of this calorimeter, viz, single readings of inlet and outlet water thermometers and the measurement of the water flowing through the calorimeter during a fractional part of a turn of the index of the meter, does not permit of accuracy in a heating value test, for several reasons, among which may be mentioned (*a*) the time error in manipulation of the change-over device becomes too large in proportion to the short time required for the meter index to travel over, at most, 0.2 of a turn and (*b*) the amount of gas delivered during a fraction of a revolution by the wet meters furnished with these calorimeters is not proportional to said fraction of a revolution.

As the tilting bucket furnished with the calorimeter is suitable only for this method of observation, it was removed and a change-over funnel substituted. The gage glass also is not necessary unless the method of observation just referred to is followed. To insure constancy of water flow, a water supply at constant pressure must be provided external to the calorimeter, either by an overflow wier or other regulating device. With the calorimeters tested, the gage glass could not be used with the calorimeter as furnished, as the water flowing from the curved outlet tube at ordinary rates of flow drew in air through the gage glass, causing irregularity in the water flow.

In the tests made the gage glass was omitted and the outlet tube was turned through an angle slightly in excess of 90°, to permit the escape of air which otherwise accumulated in the bend of the tube.

It will be seen from Fig. 29 that in the instrument as furnished by the makers the burner is set so that the base of the flame is only a short distance above the lower boundary of the combustion chamber. On pp. 58, 59, it was shown that raising the burner 3 inches above the position indicated in Fig. 29 increased the observed heating values by about 1 per cent, while adding the radiation shields resulted in a further increase of about 0.5 per cent. In a subsequent experiment with another calorimeter the total increase in the observed heating value, due to raising the burner and to adding radiation shields, was found to be about 1 per cent. The burner should therefore be set so that the base of the flame is at least 3 inches within the combustion chamber.

With the burner raised and radiation shields added, the temperature at which the products of combustion were discharged was 3° to 4° F above that of the inlet water. The products of combustion were found to be saturated with water vapor at a temperature very approximately the same as that at which they escaped through the outlet, thus indicating that these products had not been cooled to the temperature of the inlet water. The cooling of the products is not as effective as it is in the calorimeters of the condenser-tube type already described, but the loss of heat due to this cause is relatively unimportant.

The rate of heat interchange between the calorimeter and its surroundings, when water, the temperature of which differed from the room temperature, was run through the calorimeter, with no gas burning, was found to be 0.055 Btu per minute per 1° F difference between water temperature and room temperature, i. e., about twice as great as for an air-jacketed calorimeter. It was found that wetting the wood lagging caused no appreciable difference in the rate of heat interchange.

The so-called radiation loss from the surface, when the calorimeter is operated with the inlet water at room temperature, is probably quite small, as practically the entire calorimeter with the

exception of a small part at the top is jacketed with the inlet water.

The normal rate of gas consumption for illuminating gas (650 Btu) was found to be about 7.5 cubic feet per hour, when the damper was open. The calorimeter is so constructed that only a portion of the products of combustion escape through the opening provided for that purpose, the remainder escaping through the space between the iron base-plate and the body of the calorimeter. As this opening was more or less obstructed by the asbestos and wooden lagging, the normal rate might have been different if the lagging had been slightly displaced.

The calorimeter is so designed and constructed that the drainage of the water formed by the condensation of aqueous vapor from the products of combustion is fairly regular, although improvement in this respect is desirable if net heating values are to be calculated from the amount of condensate delivered during the time that a small quantity of gas (about 1 cubic foot) is burned in the calorimeter.

The bulb of the outlet-water thermometer is surrounded by a perforated metal cone, apex downward. With this device in position the thermometer did not indicate the true mean temperature of the effluent water, as was shown in the experiments cited on p. 51. Accordingly a mixing device consisting of several baffle plates was substituted for the perforated cone. A mixing device similar to that made for the new type Junkers calorimeter would have been preferable, although the baffle-plate mixer proved satisfactory. With this mixer in position the efficiency of the calorimeter as a heat absorber, as determined from experiments with the electric heating coil, was found to be over 0.996.

The lag of the calorimeter is greater than that of the Junkers, Hinman and Sargent calorimeters, but is considerably less than that of the Boys calorimeter, as was shown on p. 83. On account of the large water content of this calorimeter (14 pounds), it is some three minutes after a change of temperature of the inlet water takes place before such change makes itself evident at the outlet-water thermometer, when the calorimeter is operated at normal rate of gas consumption for illuminating gas and with a rate of water flow such as to give 18° F rise in temperature of the outlet water.

On account of the large water content and also on account of the insulating material on the outside, which is in good thermal communication with the water flowing through the calorimeter, changes in the temperature of the inlet water will introduce greater errors into the results than in the case of the other calorimeters considered in this report. For the satisfactory use of this calorimeter a supply of water at constant temperature and sufficient for at least 30 minutes' operation, should be available.

Measurement of Total Heating Value.—A Simmance-Abady (English type) calorimeter (No. 1631) was used to measure the total heating value of a sample of illuminating gas. The total heating value of this sample was determined as described on p. 110. The Simmance-Abady calorimeter was operated under the following conditions: With inlet water at constant temperature, with normal rate of gas consumption (7.5 cubic feet per hour), with burner provided with radiation shields and raised 3 inches above the position indicated in Fig. 29, and with a baffle-plate mixer in the outlet-water tube. The result of this determination showed that, if the observed heating value found with the Simmance-Abady calorimeter were corrected for the effect of atmospheric humidity (by Table 19), etc., the total heating values thus found were in agreement (0.2 per cent), to well within the limits of experimental error, with the total heating value that had been found for the gas used in the tests.

NOTE.—Most of the criticisms that have been made relate to minor defects that are quite easily corrected by simple modifications in construction, e. g., the burner may be raised, a mixing device for the outlet water provided, the tilting bucket removed, etc. It will be seen that when these changes were made and when a water supply at constant temperature was used accurate results were obtained with this calorimeter.

6. BOYS CALORIMETER [22]

This calorimeter is illustrated in Figs. 30 and 31. The water enters at the top of the calorimeter, flows downward past the bulb of the inlet-water thermometer, then through five turns of copper pipe, having a helix of copper wire would on and sweated to the

[22] C. V. Boys, Proc. Roy. Soc., London, A-77, p. 122: 1906.

surface, after the manner of some motor-car radiators, to facilitate heat interchange between the combustion products on the outside and the water within the tube, then upward through four turns of similar radiator tubing, within and concentric with the first, and separated therefrom by an insulating brattice, Q. The water then passes through several turns of copper pipe wound on and sweated to the outer cylindrical surface of a bell-shaped brass casting forming the upper part of the combustion chamber, thence into a brass box which forms the upper part of the aforesaid casting and in which is a temperature-equalizing device consisting of two dished plates of thin brass, K K, held in place by three scrolls of thin brass, L L L, thence into the outlet tube, in which is found the bulb of the outlet-water thermometer, and thence is discharged from the calorimeter. The parts described are supported from a wooden top, G. Surrounding the outer turns of the radiator coil is a cylindrical mantle of thin sheet metal, which is also supported from the wooden top and which serves to protect the radiator coils and to support the calorimeter when the latter is removed from the outer casing, D. The total capacity of the water circulation system is small, the water content being only about 0.7 pound (300 cc).

The annular space between the outer casing, D, and the metal chimney, E, is closed at the bottom and is filled to a depth of about 1 inch with water (about a pound), in which the lower turns of the radiator coils are immersed. The level of the upper surface of this water is fixed by the position of the small drain tube, F, and the water condensed from the products of combustion is drained off through this tube.

The calorimeter rests on three metal supports, C, at a small distance above the metal plate which covers the wooden base, A, in which the double union jet (luminous flame) burner, B, is mounted.

The products of combustion pass upward through the metal chimney, E, impinge against the brass box, H, through which water is circulated and which forms the top of the combustion chamber, thence downward past the inner turns of the radiator coils, upward on the outside of the brattice, Q, past the outer turns of the radiator coils and out of the calorimeter through a number of holes in the wooden top, G. There is also an opening in this top

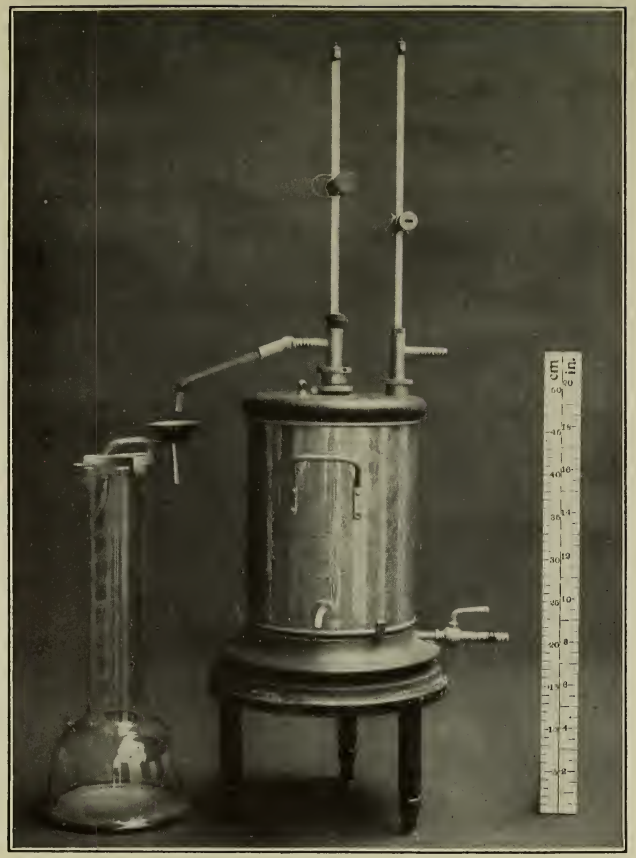


Fig. 30

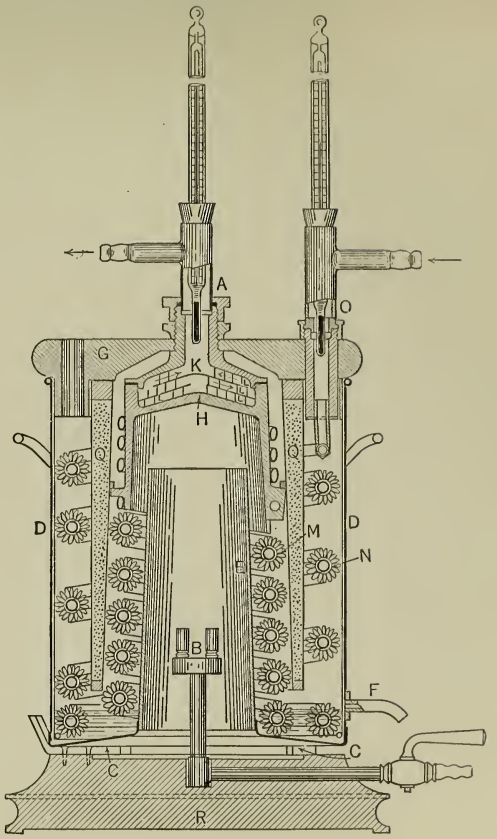


Fig. 31

Boys calorimeter (John J. Griffin & Sons)

for the thermometer intended for measuring the temperature of the outlet products. The various parts of the water circulation system are connected by union joints, so that the sections can be readily taken apart. To prevent corrosion, the calorimeter, when not in use, is lifted from its base and set into a jar containing a solution of sodium carbonate.

One of the features which the designer particularly emphasizes is that the water flows through the calorimeter in series, thus avoiding the fluctuations in the readings of the outlet-water thermometer due to insufficient mixing of unequally heated parallel streams of water.

Special Tests.—When the luminous flame burner was used and the rate of gas consumption was 4.7 cubic feet per hour, incomplete combustion set in, as was made evident by the appearance of black smoke in the products of combustion. This proved to be a very sensitive test of the occurrence of incomplete combustion, as very evident traces of smoke could be seen before the observed heating value had been diminished by 0.5 per cent. The normal rate of gas consumption for this calorimeter and for the illuminating gas tested (650 Btu) was about 3.3 cubic feet per hour.

The products thermometer, as it is mounted in this calorimeter in a small hole closed with a cork, can hardly be expected to give a reliable indication of the temperature of the products, as there is but little circulation of the products past the bulb. If the thermometer is inserted so that the bulb is below the bottom of the wooden cover it is brought into contact with the radiator coils. When mounted in a cork in the hole provided for this purpose, the products thermometer indicated a temperature about 5° to 6° F above that of the inlet water, while the actual temperature of the products, as indicated by a thermometer mounted with its bulb in one of the larger outlet product holes, so that the products flowed past the bulb, was only about 3° F above that of the inlet water.

The gain or loss of heat due to a difference of 1° C (1°.8 F) between the temperatures of the surrounding air and of the escaping products of combustion, is very small, apparently much smaller than is indicated in the rule given by Boys, viz, "The correction

for rise or fall of temperature of the air passing through the instrument is as near as possible one-third (or one-sixth in later publications) of a calorie to the cubic foot of gas for each 1° C of change." The assumption made in the deduction of this rule was that the ratio of volumes air to gas was about 8¼ to 1. A simple computation [23] shows that under the above conditions the gain or loss of sensible heat is more nearly one-sixteenth Calorie instead of one-third (or one-sixth) Calorie to the cubic foot of gas for each 1° C of change. If the gain or loss of heat due to the difference in the amounts of water vapor carried into and out of the calorimeter is considered, the correction depends not only upon the volumes and the temperatures but also upon the degrees of saturation of the entering air (and gas) and of the escaping products, and is not proportional merely to the difference in the temperatures of air and products.

The time required for this calorimeter to attain thermal equilibrium after lighting the gas or after any change in the rate of heat supply to the calorimeter has taken place (e. g., due to a change in the heating value of the gas) is somewhat less than for the Simmance-Abady (American type) calorimeter, which is of very similar construction, but is greater than for any of the other flow calorimeters included in this investigation. It was pointed out on p. 83 that a small water content does not necessarily mean that the lag will be small. The large lag of this calorimeter is due to the presence of considerable amounts of poorly conducting material that enter into the construction of the calorimeter, the presence of a considerable mass of still water in the bottom of the calorimeter, and the use of a heavy metal chimney and a heavy brass casting to form the combustion chamber.

The advantage claimed for this calorimeter, that the water flows in series through the calorimeter and that the difficulties arising from insufficient mixing of parallel unequally heated streams of

---

[23] Eight and one-fourth cubic feet of air per cubic foot of gas burned correspond to about 7.8 cubic feet of products per cubic foot of gas burned. The weight of 1 liter of products is about 1.2 grams, and the specific heat is approximately 0.23. Therefore, if the products are 1° C warmer than the entering air, they will carry out an amount of sensible heat given by

$$7.8 \times 28.3 \times 1.2 \times 0.23 = 61 \text{ small calories}$$

$$= \frac{1000}{61} = \frac{1}{16} \text{ large calorie.}$$

In the above computation a number of minor factors have been neglected. A complete analysis of all the heat interchanges involved is given in previous sections of this report.

water are thus obviated, might be expected from theoretical considerations, yet the fact remains that the application of the principle, on account of the presence of certain sources of error in the two calorimeters in which it has been applied, has not resulted in a calorimeter of as high accuracy as the parallel flow calorimeters. The readings of the outlet-water thermometer, it is true, are not subject to as large fluctuations as are the readings of the outlet-water thermometers of the other calorimeters, but this is undoubtedly in part due to the large lag of this calorimeter, which is less sensitive to sudden variations in the rate of heat supply.

The drainage of the water formed by the condensation of aqueous vapor from the products of combustion was frequently very irregular, as is to be expected where the drainage takes place from the top of a water surface of large area, even when precautions were taken to prevent contact between the outer casing and the metal shield around the radiator coils.

The experiments on the efficiency of this calorimeter as a heat absorber, as determined with an electric heating coil mounted in the combustion chamber, did not lead to satisfactory results as was explained on p. 51, but served to indicate that the efficiency was lower than for the other calorimeters on account of the favorable conditions for conduction of heat to the base and other parts of the calorimeter. This conclusion was corroborated by the results of the experiments summarized below.

Determination of Total Heating Value.—The total heating value of a given sample of gas was determined as described on p. 110. The Boys calorimeter No. 67 was then used to measure the heating value of the same sample of gas. The data of such a test are given in Table 29. It will be seen from this table that the heating values found with the Boys calorimeter are about 2 per cent low. A similar series of tests made August 1, 1912, gave practically the same result (1.8 per cent).

The net heating values determined by the two calorimeters, if calculated from the data given in Table 29 and footnote c, would be in fairly good agreement, but this is due to the abnormally small volume of condensate delivered by the Boys calorimeter in this test. In the test of August 1, 1912, the volume of condensate delivered by the Boys calorimeter was about 1 cc per cubic foot

of gas greater than that delivered by the Junkers calorimeter, so that the net heating value found with the Boys calorimeter in that test was over 2 per cent low.

The heat losses from this calorimeter were appreciably reduced by the following changes: (*a*) The substitution of a porcelain stem Bunsen burner for the luminous flame burner furnished with the calorimeter; (*b*) the separation of the sheet-metal bottom from the wooden base on which it rests by interposing three small insulating blocks. The addition of radiation shields to the porcelain stem Bunsen burner caused no further certain diminution in heat loss. When the Bunsen burner was used the normal rate of gas consumption depended to a considerable extent upon the character of the flame—e. g., by making the flame strongly oxidizing the normal rate could be increased to 5 or 6 cubic feet per hour. When the Bunsen burner was adjusted to make the normal rate 3.5 cubic feet per hour, the heating values found with the calorimeter were still over 1 per cent low.

In an editorial notice in the London Journal of Gas Lighting for April 14, 1914, the question was raised as to whether the conclusion reached by the authors, viz, that the Boys calorimeter No. 67 gave heating values about 2 per cent low, was applicable to the Boys calorimeter as a type, or whether the instrument tested was defective. Since that date a further and most exhaustive series of tests has been made on the Boys calorimeter No. 67 and on another Boys calorimeter, No. 60, loaned by Mr. J. B. Klumpp. Alternate measurements were made with the Junkers calorimeter No. 1209 and with the Boys calorimeters on the same sample of gas drawn from a holder. The same meter was used, thus diminishing the errors of metering; furthermore, in some of the tests the same pair of thermometers was used in all the calorimeters. The results of a large series of such tests again gave the result that the observed heating values found with the Boys calorimeter No. 67 were 2 per cent lower than those found with the Junkers calorimeter, while the absorbed heating values found with the Boys calorimeter No. 60 were over 1 per cent lower.

The lower values found with the Boys calorimeter No. 67 were due in part at least to the fact that a relatively small part of its radiator coils was immersed in the still water in the bottom of the

calorimeter, with the result that this water became appreciably heated during the operation of the calorimeter. Calorimeter No. 67 had 9½ turns of radiator coil while No. 60 had 10 such turns.

TABLE 29

Comparison of Boys Calorimeter No. 67 with Junkers Calorimeter No. 1209 (Sept. 3, 1913)

Experiment No.	1	2	3	4	5	6
Calorimeter	Junkers No. 1209		Boys No. 67		Junkers No. 1209	
Time of beginning test	2–51	2–54	[a] 3–13	3–19	3–40	3–44
Room temperature	81°	81°	82°	82°	82°	82°
Atmospheric humidity	68%	.....	67%	.....	68%	.....
Products temperature	82°	82°	[b] 87°	[b] 87°	82°	82°
Condensate for 1 cu. ft. gas	19.6 cc		erratic [c]		19.8 cc	
Rate of gas consumption [d]	6.9	6.9	3.2	3.2	6.8	6.8
Temperature of inlet water, corrected	82°04	82.04	82°00	82.00	81°95	81.95
Temperature of outlet water, corrected	100°38	100°38	100°40	100.40	100°00	100°00
Temperature difference	18°34	18°34	18°40	18.40	18°05	18°05
Water collected, pounds	6.459	6.462	6.327	6.332	6.574	6.585
Volume of gas at 60° F, 30 ins.	0.1900	0.1900	0.1899	0.1899	0.1898	0.1898
Observed heating value, Btu	623.4	623.8	613.0	613.5	625.2	626.2
Correction for radiation	+0.6	+0.6	(e)	(e)	+0.6	+0.6
Correction for sens. heat of products	.....	.....	+0.6	+0.6	.....	.....
Correction for (inlet minus room) temperature [f]	+0.4	+0.4	0.0	0.0	0.0	0.0
Correction for latent heat of condensate	−45.1	−45.1	.....	.....	−45.5	−45.5
Net heating value, Btu	579	580	.....	.....	580	581
Observed heating value, Btu	623.4	623.8	613.0	613.5	625.2	626.2
Correction for radiation	+0.6	+0.6	.....	.....	+0.6	+0.6
Correction for sens. heat of products	.....	.....	+0.6	+0.6	.....	.....
Correction for (inlet minus room) temperature [f]	+0.8	+0.8	0.0	0.0	0.0	0.0
Correction for atmospheric humidity [g]	+2	+2	+2	+2	+2	+2
Total heating value, Btu	627	627	616	616	628	629

[a] The Boys calorimeter had been in operation over an hour on a separate supply of gas, giving the same temperature rise, and was switched over to gas under test without extinguishing the flame.

[b] Reading of thermometer mounted in cork in hole in cover of calorimeter.

[c] Condensate collected was 16 cc. Evidently too little.

[d] The rate of gas consumption was the normal rate for each calorimeter.

[e] The several corrections for heat losses to surroundings were not determined separately for this calorimeter. The results of this and other tests show that these heat losses amount to about 11 or 12 Btu, i. e., nearly 2 per cent.

[f] Correction for difference between inlet water and room temperatures taken from Table 21.

[g] Correction for effect of atmospheric humidity taken from Table 19.

Further experiments with other Boys calorimeters are planned, and the results will probably be published in the Journal of Gas Lighting.

7. SIMMANCE-ABADY CALORIMETER (AMERICAN TYPE) [24]

Description.—The calorimeter is illustrated in Figs. 32 and 33. As will be seen from the illustration, features of the Boys and Simance-Abady (English type) calorimeters have been incorporated into this instrument. The water enters the tube, in which is placed the bulb of the inlet-water thermometer, at the top of the calorimeter, flows downward in an annular space and then upward in a spirally wound radiator coil, thence through several turns of copper pipe wound on and sweated to the outer cylindrical surface of a bell-shaped brass casting forming the upper part of the combustion chamber, thence into a brass box which forms the upper part of the aforesaid casting, and in which is a temperature equalizing device similar to that used in the Boys calorimeter, thence into the outlet tube in which is placed the bulb of the outlet-water thermometer. After passing the bulb of the outlet-water thermometer, the water is led to another upright tube in which is supported a gage glass, and then is discharged from the calorimeter through a curved tube into a tilting bucket. The gage glass, outlet tube, and tilting bucket are the same as are used in the English type Simmance-Abady calorimeter, and the discussion of these features in the section relating to that calorimeter is also applicable to this instrument. The annular water space is surrounded by a casing of thin sheet metal inclosing a narrow air space. The various connections in the calorimeter are made with union joints, so that it can be taken apart for cleaning or repairs.

The products of combustion pass upward in the combustion chamber, which is formed by a heavy metal tube, impinge against the water-cooled casting at the top, flow downward past the radiator coils in the space between the combustion chamber and the outer annular water space, and are discharged from the calorimeter through an opening provided with an adjustable damper.

Special Tests.—On page 58 it was shown that by using a longer burner stem, so that the base of the flame was about 4 inches above the lowest line of water circulation, the observed heating values were increased by over 1 per cent, and that the use of shields on the burner, in its raised position, resulted in a further increase of several tenths of 1 per cent. With the burner raised and shielded,

[24] The calorimeter tested was kindly loaned for this investigation by the Precision Instrument Co.

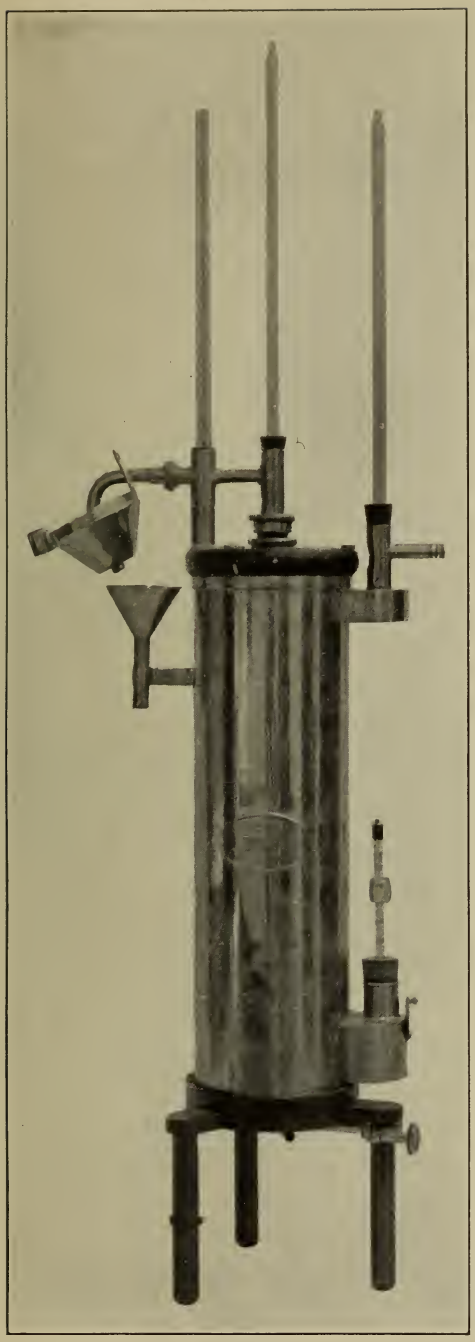


Fig. 32

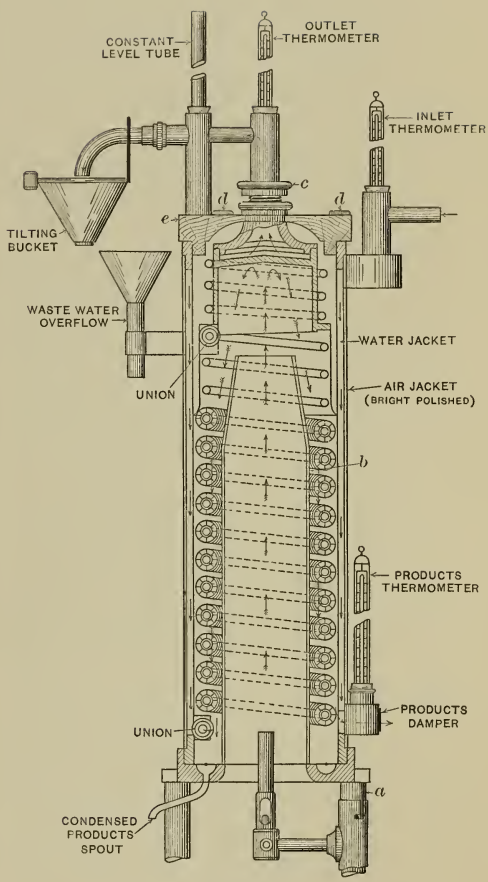


Fig. 33

Simmance-Abady calorimeter (American type)

the temperature at which the products of combustion were discharged was about 6° F above that of the inlet water when the combustion chamber consisted of the heavy metal tube with which the calorimeter was provided. When a light metal tube was substituted, the excess of temperature was reduced to 1.5° F. The rate of heat interchange between the calorimeter and its surroundings, when water, the temperature of which differed from that of the room, was run through the calorimeter, with no gas burning, was found to be about 0.05 Btu per minute per 1° F difference between water temperature and room temperature. The so-called radiation loss from the outer surface, when the calorimeter is operated with the inlet water at room temperature, is probably quite small, as nearly the entire calorimeter is jacketed with the inlet water.

The normal rate of gas consumption for illuminating gas (650 Btu) was found to be about 3.5 cubic feet per hour when the damper was open.

The calorimeter is so designed and constructed that the drainage from it, of the water formed by the condensation of aqueous vapor from the products of combustion, is fairly regular, so that the heat imparted to the calorimeter by the condensation of water vapor can be accurately determined. Net heating values can therefore be determined with this calorimeter as accurately as can total heating values (see below).

On page 86 it was shown that the lag of this calorimeter was greater than that of any of the other calorimeters tested, due in part to conduction of heat to the metal base of the calorimeter by the heavy metal tube forming part of the combustion chamber. When a light metal tube was substituted the lag was considerably reduced.

The efficiency of this calorimeter as a heat absorber, as measured with an electric heating coil in the combustion chamber, was about 0.99, the somewhat lower efficiency than that of other calorimeters being undoubtedly due, in part, to the conduction of heat to the metal base of the calorimeter through the heavy metal tube forming part of the combustion chamber.

Determinations of Heating Values.—Two calorimeters of this type were tested. The total heating value of a given sample of

gas was determined as described on page 110. The calorimeter under test, with burner raised and provided with radiation shields, was then used to determine the heating value of the same sample of gas. When the combustion chamber consisted of the heavy metal tube (2.6 pounds), the heating values found with this calorimeter were about 1 per cent low. When a light metal tube (0.27 pound) was substituted, the heating values found were less than 0.5 per cent low.

8. DOHERTY CALORIMETER [25]

Description.—The principle on which the action of this calorimeter is based may be briefly described as follows: The calorimeter proper is similar in principle to the other flow calorimeters, the heat generated by the combustion of the gas in a Bunsen burner being imparted to a stream of water flowing through the surrounding calorimeter. The water after leaving the calorimeter enters a tank which contains the sample of gas to be tested, and thereby displaces through the burner a volume of gas equal to the volume of water passed through the calorimeter, provided that the temperature of the gas remains uniform and constant throughout. The uncorrected heating value in Btu per cubic foot of gas, measured at the temperature and pressure existing in the gas tank, is found by multiplying the rise in temperature of the water by the number of pounds in a cubic foot of water at the outlet water temperature.[26] The heating value so obtained is then corrected to the standard conditions for measurement of gas (60° F, 30 inches) to find the observed heating value as defined on page 14. The volume of gas burned being equal to the volume of water heated, it is not necessary to measure these volumes independently; so that the use of the gas meter and the weighing of the water, necessary with the usual type of flow calorimeter, is dispensed with. A calorimeter operating on this principle would seem to be adapted for use as a recording calorimeter, as it automatically maintains a constant ratio of volume of gas to volume of water; so that only changes in the heating value or in the tem-

[25] The calorimeter No. 16 was kindly loaned for this investigation by the Improved Equipment Co.

[26] Inasmuch as the water is measured volumetrically, the heat capacity of a cubic foot of water for various outlet-water temperatures may be found, without sensible error, by multiplying the weight of a cubic foot of water at 60° F, viz, 62.4 pounds, by the appropriate factor taken from Table 22, p. 91.

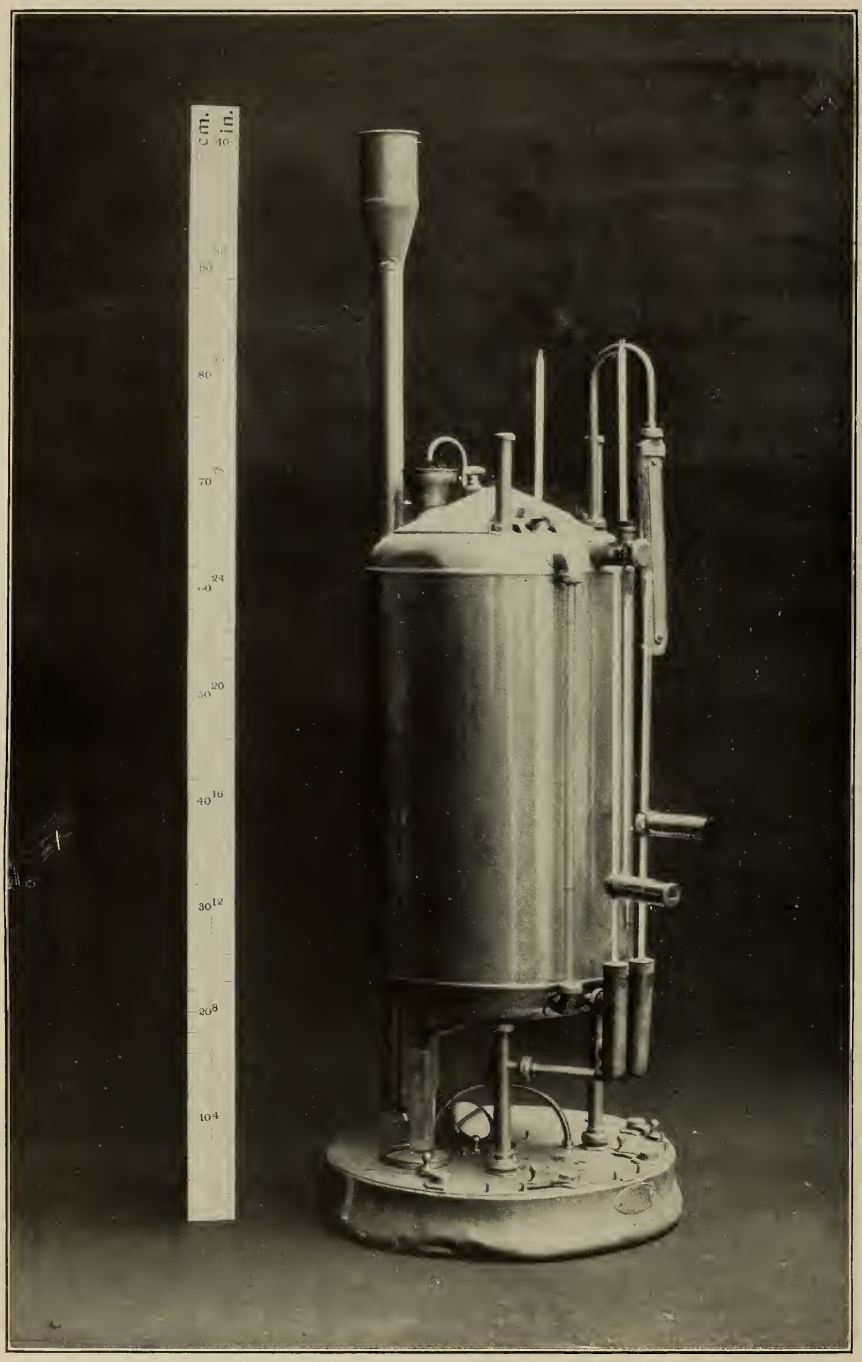


Fig. 34.—*Doherty calorimeter*

perature or in the pressure of the gas produce changes in the temperature rise of the water flowing through the calorimeter. Arrangements would have to be made for automatically refilling the tank with gas, and if only one tank were used the record would be discontinuous. In a recording instrument the two thermometers would of course be replaced by a differential mechanical or electrical thermometric device combined with a suitable recorder.

The calorimeter is shown in Fig. 34. The internal connections are too complicated to be shown clearly in a single sectional drawing. For details of construction the reader is referred to the patent specifications, United States Letters Patent No. 828306. The essential principles of construction are shown in the diagrammatic sketch, Fig. 35. The water flows through the calorimeter under a pressure determined by the difference in level between the inlet wier A and the outlet wier B. The rate of flow is regulated by a throttle valve C beyond the outlet of the calorimeter. The water, passing the inlet-water thermometer I, enters the bottom of the calorimeter and flows upward in two concentric annular spaces D E, through a mixing chamber F, at the top, and down through a pipe G, between the two annular spaces, past the outlet-water thermometer O, and thence to the outlet wier B. From the outlet wier the water is discharged through a pipe H into the bottom of the gas tank K, and displaces the contained gas through the circuit leading to the Bunsen burner. The pressure of the gas in the tank is controlled by manipulating the two valves C and L, and is equal to atmospheric pressure plus the pressure shown by the manometer M. The level of the water in the gas tank is shown on the graduated gauge glass N. After all the gas is expelled from the tank and the latter is full of water the water from the calorimeter continues to discharge from the outlet wier by another passage, P, into the drain. The outlet wier is placed so that the water in the tank will not rise above the level Q and flood the gas pipes R S, leading to and from the gas tank. In the instrument, as actually constructed, the annular gas tank surrounds the calorimeter.

The Bunsen burner is placed within the inner of the two concentric annular water channels D E. The products of combustion

pass upward through the central combustion chamber T, through one of a number of openings in the top of this chamber, depending upon the position of an adjustable damper U, past a series of baffle plates in the space between the concentric water channels D and E, and are finally discharged into the air through a vent V, at the

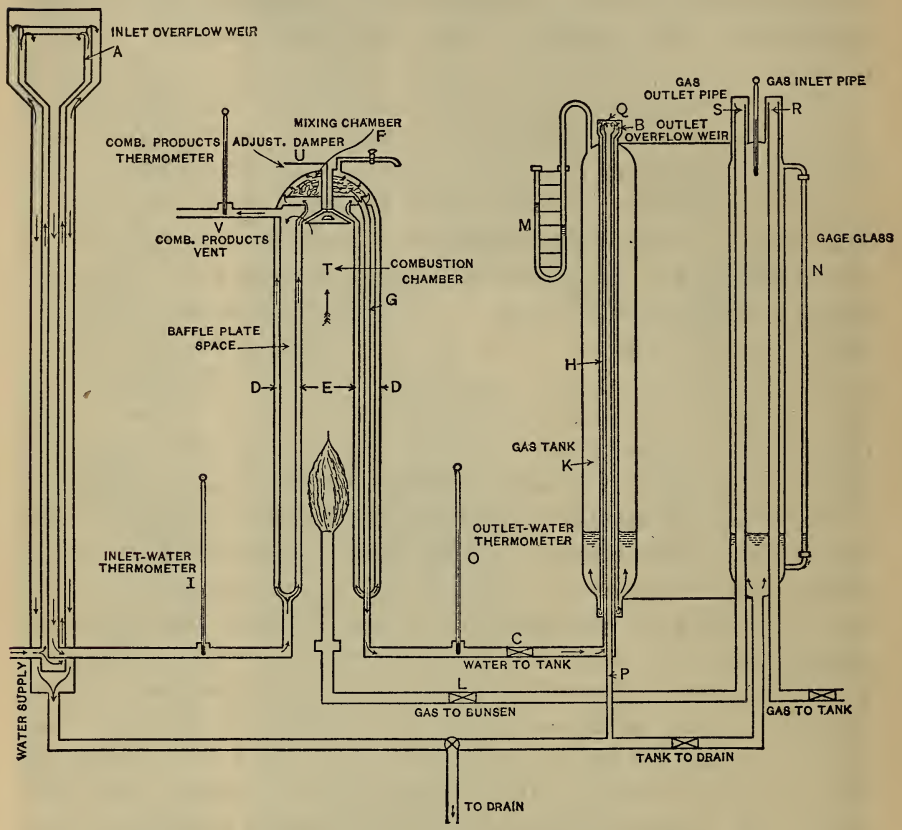


Fig. 35.—*Diagrammatic sketch illustrating construction and principle of operation of Doherty calorimeter*

top of the calorimeter, where their temperature is taken with a thermometer. The position of the damper determines the length of the path in the baffle plate space that the products of combustion must traverse, and therefore the temperature, within certain limits, at which they are discharged from the calorimeter.

On account of the complexity of connections and inacessibility of parts repairs to this calorimeter would be verv difficult to make.

Special Tests.—The first tests made consisted in a determination of the efficiency of the calorimetric part of the apparatus as a heat absorber when operated under various conditions. For this purpose the piping was disconnected just beyond the outlet-water thermometer and a rubber tube connection used to carry the water discharged from the calorimeter to a change-over funnel, thus permitting weighing of the water as with the usual flow calorimeters. The gas was supplied through a gas meter of the usual type. The calorimeter was operated at various rates of gas consumption from 1.7 to 3.7 cubic feet per hour, the damper being set to give the minimum temperature obtainable for the combustion products.

Combustion ceased to be complete at a rate of gas consumption of about 3.7 cubic feet per hour, and therefore the normal rate of gas consumption for the gas tested and for the damper setting used was about 2.6 cubic feet per hour. If the damper had been set differently, the normal rate might not have been the same, the difference depending upon the relative resistance to the flow of the combustion products around the baffle plates and through other parts of the flue spaces.

Alternate experiments were made on the same sample of gas using the burner with and without radiation shields. It was found as the result of these experiments that the loss of heat through the open bottom of the calorimeter (i. e., without shields) was less than 0.5 per cent. In view of the inconvenience in the use of shields with this calorimeter and of the presence of other errors, discussed subsequently, it was decided to omit the shields in subsequent experiments.

The calorimeter gave heating values about 1.3 per cent low, when operated as a flow calorimeter of the usual type, i. e., in connection with a gas meter, and under the following conditions: Inlet water at room temperature, surrounding gas tank empty and at room temperature, burner without shields, damper set to give maximum cooling of products of combustion, and gas burned at

normal rate. It will be shown subsequently that, with the proper method of operating the Doherty calorimeter, the lower calorimetric efficiency of the instrument tested (No. 16) was largely compensated by the gain of heat from the surrounding gas tank. The lower calorimetric efficiency is accounted for by (*a*) the high temperature of the exhaust products, (*b*) heat losses through the open bottom, and (*c*) heat losses to the surroundings, which are of relatively more consequence for this calorimeter than for calorimeters in which the rate of supply of heat is greater.

The combustion-products thermometer indicated that the temperature of the products was about that of the outlet water, but the true temperature was considerably higher, as was shown by removing the combustion-products tube and inserting a small thermometer some distance back into the horizontal space through which the products escaped. It was found that the products of combustion, when the damper was set for maximum cooling, escaped from the calorimeter saturated at a temperature about 1° F above that of the inlet water, indicating that they had been cooled down nearly to the temperature of the inlet water and then reheated before escaping at the top of the calorimeter.

This calorimeter will give somewhat different results depending upon its method of operation, due principally to the fact that the true rate at which the gas is being displaced from the gas tank will, in general, differ from the apparent rate as determined by the volume of the displacing water and from the temperature indications of the thermometer mounted in the top of the gas tank, unless the conditions of operation are such that the temperature of the gas is uniform and constant throughout.

Three methods of operation representing conditions likely to be encountered in practice were used. These were:

(*a*) With the temperature of the inlet water about 10° F below that of the room, and the outlet water therefore at room temperature, the tank having been filled with gas by displacing from it water at room temperature.

(*b*) With the temperature of the inlet water about equal to that of the room, and the outlet water which displaced the gas therefore about 10° F above room temperature, the tank having been filled with gas by displacing from it water at room temperature,

so that the tank and the contained gas were initially at room temperature.

(*c*) With the temperature of the inlet water about equal to that of the room, but the tank having been filled with gas by displacing from it water about 10° F warmer than the room temperature (outlet water), so that the tank and the contained gas were initially at a temperature above that of the room.

Method (*a*) is the ideal method of operation, in that it avoids uncertainties in the true mean temperature of the gas, the gas being initially at room temperature, and being displaced by water at room temperature, so that the errors in the measurement of the gas are minimized, and therefore observations made at various times during the progress of an experiment all lead to the same calculated heating value, which is not the case with method (*b*) (see below).

In the preliminary experiments it was found that this calorimeter when used as an ordinary flow calorimeter, gave results about 1.3 per cent low. It was also found, by running water through the calorimeter with no gas burning, but with the outer gas tank filled with water at room temperature, the inlet water being about 10° F colder, that the water was heated in its passage through the calorimeter, the outlet-water thermometer indicating a rise of temperature of 0.12° F at the rate of water flow used in the experiments. This rise of temperature was due to the heat conducted from the gas tank, through the felt insulation, to the inclosed calorimeter. In a heating-value test the amount of heat thus communicated will be somewhat less than under the conditions of the above experiment. It is evident that when the calorimeter is operated by method (*a*), the gain of heat due to operating the calorimeter with inlet water below room temperature and the resulting conduction of heat from the gas tank will tend to compensate for the effect of the lower calorimetric efficiency. It is shown in Table 30 that the compensation for the instrument tested was very close.

In method (*b*) the rate at which the gas is being displaced from the gas tank can not be correctly determined by the volume of the displacing water and from the indications of the thermometer in the gas tank. The gage glass on the front of the calorimeter

shows the level of the water in the gas tank. The lowest graduation of this glass is so placed that about one-fourth of the volume of gas in the tank is burned before the meniscus showing the water level reaches this graduation, during which interval the calorimeter is coming to an equilibrium condition. Inlet and outlet water thermometer readings, made at frequent intervals while the meniscus was moving over the entire graduated scale of the gage glass, were divided into three groups, corresponding to the first, middle, and last three graduation intervals. When these three groups of readings were used separately to calculate the heating value, on the assumption that the reading of the thermometer in the top of the gas tank gave the temperature of the gas, it was found that the first group gave a value 0.6 per cent higher than the middle group and 1 per cent higher than the last group of observations. The mean heating value, calculated from readings taken while the meniscus traversed the entire graduated part of the gauge glass, was about 0.8 per cent lower than the heating value found when the calorimeter was operated by method (*a*), as is shown in Table 30.

In method (*c*) the inlet water was at room temperature, but the gas tank, initially filled with water about 10° F above room temperature (outlet water temperature), was filled with gas as rapidly as possible by displacing the warm water, and the calorimetric experiment was begun immediately. Under these conditions of operation, as may be seen from Table 30, the heating value found was about 1.2 per cent lower than when the calorimeter was operated by method (*a*). As in method (*a*), the heating values calculated from observations made while the meniscus was at different positions in the gage glass did not differ appreciably. If the calorimetric experiment had not been started until some time after the tank had been filled with gas, the tank and contained gas would have attained the room temperature, and method (*c*) would have become identical with method (*b*).

The Doherty calorimeter is not so well adapted to the accurate determination of net heating values as is a flow calorimeter of the usual type.

Total Heating Value.—The method by which observed heating values, found with the usual type of flow calorimeter, may be cor-

rected to total heating values has been considered in previous sections of this report. The reduction of observed heating values obtained with the Doherty calorimeter to total heating values involves so large a number of separate factors that it would require an elaborate series of experiments to determine the magnitude of each of the factors separately. It can readily be shown that if the observed heating values obtained with the Doherty calorimeter are in agreement with those obtained with a flow calorimeter of the ordinary type, at a given atmospheric temperature and humidity, they will also be in agreement at all other humidities and at all temperatures ordinarily prevailing in the laboratory. It may be seen from Table 30 that when the Doherty calorimeter No. 16 was operated according to method (*a*), described above, the observed heating values found were in agreement with those found with Junkers calorimeter No. 1209. If this result is true in general for this type of calorimeter, the corrections for effect of atmospheric humidity, given in Tables 19 and 20, may be applied to the observed heating values found with the Doherty calorimeter, although the basis for this procedure is purely empirical. For example, for the tests summarized in Table 30 the average room temperature and humidity were 80° F and 40 per cent, respectively. The corresponding correction from Table 19 is +5 Btu, and hence the total heating value = 660 + 5 = 665 Btu.

TABLE 30

Comparison of Doherty Calorimeter No. 16 with Junkers Calorimeter No. 1209

Calorimeter	Method of operation	Observed heating value
		Btu
Junkers	Operated at normal rate, with radiation shields on burner, inlet water at room temperature.	660
Doherty	Method (a)—Operated at normal rate, damper set for maximum cooling, no radiation shields on burner, inlet water 10° F below room temperature, outlet water at room temperature.	660
Doherty	Method (b) [a]	655
Doherty	Method (c) [a]	652

[a] See text.

9. PARR GAS CALORIMETER

Description.—This calorimeter, illustrated in Figs. 36 and 37, is of the comparison type, viz, the heating value of the gas under test is compared with that of a gas the heating value of which is known. In the Parr calorimeter the comparison of heating values is made by comparing the rise in temperature in two as nearly as possible identical calorimeters, in one of which the gas to be tested is burned, and in the other of which an equal volume, or a multiple or submultiple of this volume, of the gas of known heating value is burned, the gases being displaced under the same pressure from cylinders kept at the same temperature. The relative volumes of the two gases are chosen so as to cause, as nearly as possible, equal rises of temperature in the two calorimeters. Hydrogen is used as the gas of known heating value. If ordinary illuminating gas (600 Btu) is to be tested, then, since the heat of combustion of hydrogen is a little more than one-half that of the illuminating gas, two volumes of hydrogen are burned for each volume of illuminating gas. The calorimeter is provided with three similar gas cylinders of equal volumes, of which two may be connected in parallel, so that the ratios of volumes, 2:1, 1:1, and 1:2, may be obtained. These gas cylinders are contained in a water bath immediately under the pair of calorimeters. The gas is displaced from the cylinders by water from an elevated tank, so that the pressure on the two gases is the same if the water level in the gas cylinders is the same. The water levels in the gas cylinders are indicated on two gage glasses, and these levels, the differences of which at the beginning and end of a test determine the amounts of gas burned, are controlled by two needle valves, which are used to regulate the flow of gas to the burners. There is a needle valve above each of the gage glasses to permit the escape of air when the cylinders are filled with water, previous to drawing in the gases by running out the water, and to permit of adjusting the amount of gas in each cylinder, so that the water levels in the respective gage glasses shall be the same at the beginning of a test.

The calorimeters are two similar vessels of as nearly as possible equal capacities for heat. The water circulation in the two calorimeters is maintained by stirrers of the screw propeller type,

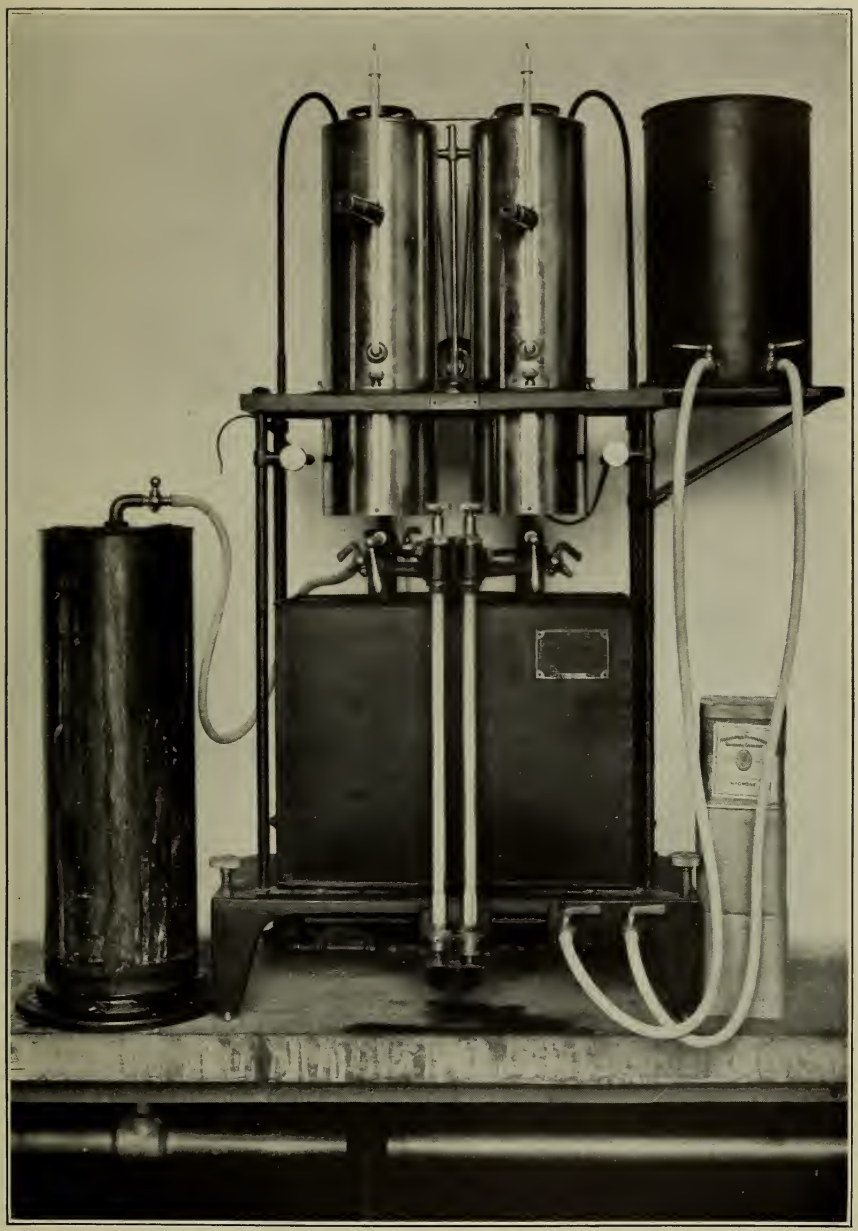


Fig. 36.—*Parr gas calorimeter*

the two stirrers being driven by a single belt from the pulley of a small motor. Each stirrer causes the water to circulate upward in a central tube, which is closed at the bottom, and which extends from about 1 inch below the surface of the water to within 3 inches of the bottom of the calorimeter. The water then flows

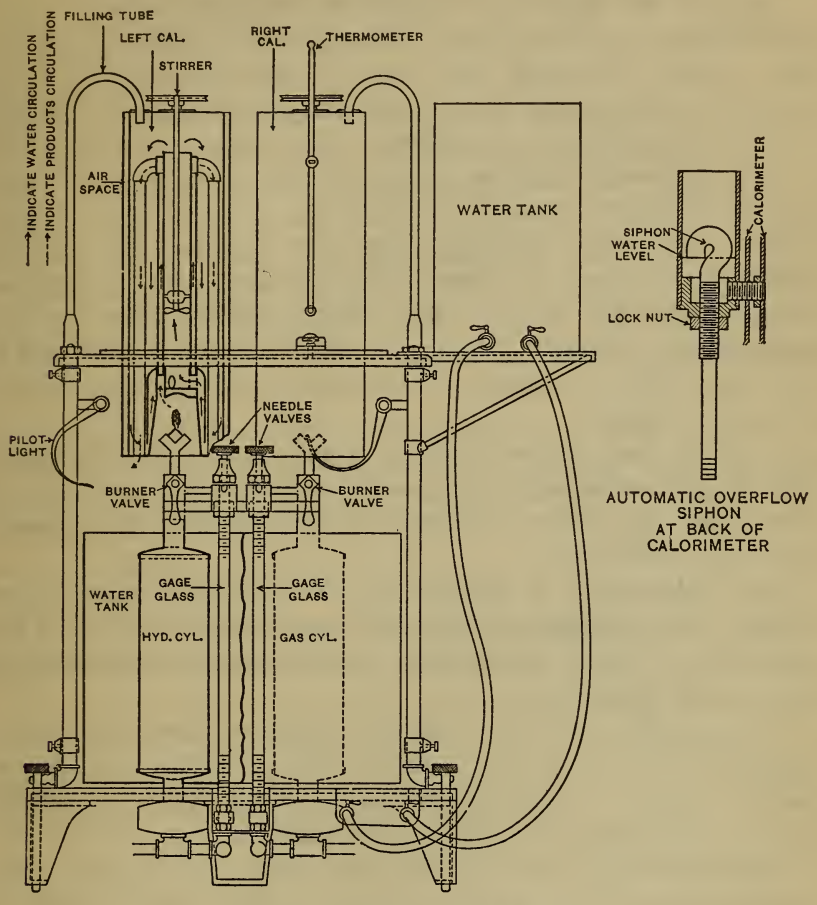


Fig. 37.—*Parr gas calorimeter (section)*

outward at the top and downward to the bottom of the calorimeter in an annular space in which is a set of condenser tubes to carry the descending products of combustion, thence upward a short distance around a partition and back into the lower portion of the central tube through three radial passages extending horizontally

across the combustion chamber. The level of the water in each calorimeter is determined by an automatic overflow siphon, which is adjustable so that the water equivalents of the two calorimeters can be adjusted to equality. The calorimeter stand is provided with leveling screws and with a circular spirit level.

The gases are burned in one-half foot acetylene burners, which are located in the lower parts of the respective combustion chambers. At the beginning of a test the gases are ignited at the burners by small pilot flames that can be momentarily turned into position under the calorimeters. The products of combustion in each calorimeter impinge against the closed bottom of the inner tube of the water circulation system and against the three horizontal radial water passages, then pass upward, through the interspaces between the three radial passages, into an annular space between the central water column and the outer annular water column, thence downward through the tubes immersed in the water of the outer annular water column, and out at the bottom of the calorimeter.

An angle stem thermometer is mounted in each calorimeter with its horizontal bulb in the outer annular water space of the calorimeter, the short horizontal portion of the stem passing through a stuffing box.

Each calorimeter is inclosed in an externally nickel-plated cylinder which incloses a narrow air space between itself and the calorimeter. Water connections are provided for renewing the water in the calorimeters.

Hydrogen is produced in a special generator shown in the photograph of Fig. 36, by the action of water on hydrone, an alloy of sodium and lead. The analyses that have been published indicate that the hydrogen so obtained is very pure.[27]

This calorimeter is not intended for and is not adapted to the determination of net heating values. No provision is made for collecting the condensate; indeed, some of the water condensed in the combustion chamber occasionally drops down on the burners.

In the use of this calorimeter care must be exercised to insure that the hydrogen delivered by the generator is not contaminated

[27] Report of Calorimetry Committee American Gas Institute 1912.

with other gases. Care must also be exercised to obtain an average sample of the gas to be tested and to avoid the introduction of air while filling the cylinders. In igniting the gas at the beginning of the test no gas should be allowed to escape unburned. If the gas does not ignite at the first trial, the cylinders must be refilled and the test started again. On account of the small volume of gas burned in a test the presence of even small leaks may cause appreciable errors. The results obtained in the determination of the total heating value of the same sample of gas with the Parr calorimeter and with the Junkers calorimeter (see Table 33) do not indicate that any appreciable error was introduced into the results obtained with the Parr calorimeter, due to the absorption of constituents of the illuminating gas by the water which displaced this gas or to the contamination of either the hydrogen or the illuminating gas by gases liberated from the water. No special experiments were made to directly test whether such effects existed.

The pilot lights can not be operated so as to produce heat at the rate of less than about 1 Btu per minute for each. The total amount of heat produced by the combustion of the gas in a test of illuminating gas is only about 30 Btu for each calorimeter. It is evident, therefore, that these lights should be made as nearly equal and as small as possible without danger of extinguishing them in use, and they should be so manipulated in lighting the gases that the difference in the amount of heat thus introduced under the one or the other of the calorimeters is negligible in comparison with the heat imparted to each calorimeter. For example, with pilot lights that produce 1 Btu per minute, if one of these lights were left under one calorimeter six seconds longer than the other pilot light, the difference in the amount of heat thus introduced under the calorimeters would be 0.1 Btu, which would introduce an error of about 0.3 per cent in the heating value found from the test.

The time required for a single heating value determination with the Parr calorimeter is probably not very different from the time required with a flow calorimeter. A series of determinations, however, can be obtained in considerably less time with a flow calorimeter.

The effect of slow deterioration in the heating value of illuminating gas, due to standing for a long time in the cylinders in contact with water, or the deterioration of samples which may be collected and subsequently tested, will depend upon the chemical constitution of the gas and is of the same nature as that discussed on page 98.

Special Tests.—The calorimeter tested, No. 2, was found to be in very good adjustment, with the exception that the volume of one of the three gas cylinders was about 2 per cent less than that of each of the other two. The volumes corresponding to one division of the gage glasses were determined for each gas cylinder and for the two cylinders in parallel, so that in case the position of the water in the two gage glasses was not the same at the end of a test the necessary correction could be applied. The weights of the two calorimeters, as well as their water contents, were found to be equal to within 0.1 per cent.

In all the experiments made with this apparatus calorimetric thermometers, inserted into the outer annular water spaces through openings in the tops of the calorimeters, were used instead of the angle stem thermometers mounted in the calorimeters, as there was some doubt as to whether the bulbs of the angle stem thermometers could be sufficiently immersed to avoid the effects of heat conduction.

The times of reading the initial and the final temperature of each calorimeter should be so chosen that the heat interchange with the surroundings in the interval between these times, due to conduction, convection, and radiation, is for each calorimeter proportional to the temperature rise in each. If the initial temperatures are so chosen that the final temperature of each calorimeter will be equal to the room temperature, the time elapsing between the initial reading and the ignition of the gas should be the same for each calorimeter. As under these conditions the final temperatures are practically stationary, the exact timing of the final readings is of little importance.

The application of the emergent stem corrections to the observed readings of the thermometers may be omitted, as the errors caused thereby are automatically almost entirely eliminated.

The equality of the heat capacities of the two calorimeters was tested by burning equal volumes of the same gas in each calorimeter. To eliminate the effects of residual errors in the thermometer corrections, which may be of importance on account of the small temperature rise obtained in this apparatus, the thermometers were interchanged after each test, the mean of two such tests being entered in Table 31 as the result of a single experiment.

TABLE 31

Rise in Temperature of Left and Right Calorimeters of Parr Gas Calorimeter When Equal Volumes of the Same Gas Were Burned in Each

Experiment No.	Left calorimeter	Right calorimeter	Ratio L/R
	°F	°F	
1	4.88	4.91	0.994
2	4.96	4.95	1.002
3	4.97	4.96	1.002
4	4.99	4.95	1.008
Mean	.....	.....	1.002

Although the observations were made with the greatest care, using accurately standardized thermometers graduated to 0°05 F, and eliminating residual errors of calibration by interchanging the thermometers, the precision of a single determination was not very great. However, if the two calorimeters are made thermally equal and the errors of the thermometers are eliminated by interchanging them, the variations among individual determinations are, to a large extent, due to accidental rather than constant errors, so that the mean of a number of determinations should be quite accurate. The above series of experiments shows that the heat capacities of the two calorimeters were equal to within the limits of precision attained in the use of the calorimeter.

To test the effect on the ratio of heating values found when the temperature rises of the calorimeters were quite different, the volume of gas contained in two of the gas cylinders was burned under the left calorimeter, while the volume of gas contained in one cylinder was burned under the right calorimeter, the initial

temperature of each calorimeter having been so chosen that the final temperature of each was approximately equal to the room temperature. The results of such a test are summarized in Table 32.

TABLE 32

Ratio of Temperature Rises in Left and Right Calorimeters when Volumes of Gas Burned were as 2/1

Experiment No.	Left calorimeter	Right calorimeter	L/R
1	9.89	4.92	2.010
2	10.01	4.93	2.030
Mean			2.020

The observations were made on a day of high humidity (80 per cent).

It will thus be seen that the ratio of temperature rises, which should have been 2:1, was about 1 per cent in error as determined by the calorimeter operated under the unfavorable conditions specified.

As it is not necessary, except in a few cases, to operate the two calorimeters with such different temperature rises, no special experiments were made to test the effect of atmospheric humidity under such conditions of operation.

The effect of variations in atmospheric humidity on the results is probably negligible when the calorimeter is operated so that the rise of temperature of the two calorimeters is nearly the same, but may become appreciable if the temperature rise of one calorimeter is considerably larger than that of the other.

Measurement of Total Heating Value.—The Parr calorimeter (No. 2) was applied to the measurement of the total heating value of illuminating gas. For this purpose the two gas cylinders of the left calorimeter were filled with hydrogen. The gas cylinder of the right calorimeter was filled with the illuminating gas to be tested, which was drawn from the 5 cubic foot gas holder. By means of a T connection, gas from the gas holder could be led either to the gas cylinder of the calorimeter or to a Bunsen burner. Before starting to fill the cylinder, a considerable volume of the gas

was burned in the Bunsen burner, which was also kept burning while the cylinder was being filled. The initial temperature of each calorimeter was so adjusted that the final temperatures attained were approximately equal to the room temperature.

The results summarized in Table 33 were obtained in the determination of the total heating values of two different samples of illuminating gas, with the Parr (No. 2) and the Junkers (No. 1209) calorimeters.

TABLE 33

Intercomparison of Parr and Junkers Calorimeters

Date	Parr calorimeter No. 2		Junkers calorimeter No. 1209
	Ratio illuminating gas/H	Btu of illuminating gas. H=321	
			Btu
Aug. 30, 1912, sample No. 1..	2.122	681	680
Aug. 31, 1912, sample No. 2..	2.137	686	688

The heating value to be assigned to the two samples of illuminating gas, as determined by the Parr calorimeter, will depend upon the heating value adopted for hydrogen. W. A. Roth[28] has recalculated the results of the more important determinations of the heating value of hydrogen. The mean of the five determinations summarized by Roth for the heat of combustion at constant pressure, of 1 mol of hydrogen, when the hydrogen and oxygen are initially at room temperature (70° F?) and when the water formed is condensed to liquid water at room temperature, is 68700 calories. This is equivalent to 321 Btu per cubic foot of hydrogen, saturated with water vapor, and measured at 60° F and 30 inches pressure. Parr has used the value 325 Btu per cubic foot, calculated from Thomsen's value, 68360 calories per mol. The value 325 Btu evidently applies to Thomsen's value for dry hydrogen measured at 60° F and 30 inches pressure. If the total heating value ordinarily desired, viz, for gas saturated with water vapor and measured at 60° F and 30 inches pressure, is to be determined, the heating value of hydrogen measured under the same conditions, must be used in the computations.

[28] Landolt-Bornstein-Roth, Physikalisch-Chemische Tabellen, Table 198a, p. 908.

In the Parr calorimeter, the ratio of the heating value of the gas tested to that of hydrogen is determined when both gases are measured under the same conditions of temperature, saturation, and pressure. This ratio is independent of the temperature and pressure prevailing in the test. If this ratio is multiplied by the heating value of hydrogen under standard conditions of temperature, saturation, and pressure, the resulting value will be the heating value of the gas tested under the same standard conditions.

The heat unit, in terms of which the results found with the Parr calorimeter are expressed, is the unit in terms of which the heat of combustion of hydrogen is expressed. No correction need be applied for the variation with temperature of the specific heat of water (or of the calorimeters).

X. SUMMARY

After an outline of the object of the investigation, precise definitions of the heat units and of the several heats of combustion are considered. After reference to the more important types of calorimeters that have been applied to the measurement of the heating values of gases, the principle of the flow calorimeter is set forth, and an example is given showing the reductions of and corrections to the observed data that are required in order to find the total and net heating values.

The results of an experimental investigation of laboratory gas meters, showing the errors to which such meters are liable, the precautions to be observed and the accuracy attainable in their use, are given at length. It is shown that an accuracy of about 0.2 per cent may be attained if the meter is calibrated in situ at the time of use, and that the calibration may be reproduced from time to time by making suitable adjustments, to within 0.5 per cent.

The results are given of an extended series of investigations of the various factors that may affect the accuracy of heating value determinations with flow calorimeters, such as: Completeness of combustion; accuracy of the temperature measurements; the magnitudes of the various heat losses from the calorimeter, particularly as affected by the volume of the entering air and of the

products of combustion and by the atmospheric humidity; and the accuracy of measurements of the quantities of water and of gas. The effects of certain other factors, which depend upon the nature of the gas tested and are particularly noticeable in the testing of illuminating gas, are briefly considered.

The results of an extended series of experiments with natural gas and with nearly pure hydrogen and with a mixture of the two gases having about the same heating value as ordinary illuminating gas show that, when the necessary corrections for losses of heat from the surface, for the effect of atmospheric humidity, etc., were applied to the observed heating values obtained with flow calorimeters of suitable design and construction, the total heating values thus found were in agreement to about 0.3 per cent with the total heating values obtained with calorimeters of the Berthelot bomb type, provided due allowance were made for the difference between the heat of combustion at constant pressure and the heat of combustion at constant volume.

The summarized results are given of a critical investigation of eight flow calorimeters, representing types widely used in this country or abroad, and of one calorimeter of the comparison type.

The investigation has shown that several of the calorimeters investigated could be used, when proper precautions were observed and suitable corrections were applied to the observed heating values obtained with them, to determine the total heating values of most kinds of gases to an accuracy of about 0.3 per cent. Some of the calorimeters are, however, subject to constant errors that can not be eliminated or be readily determined except by comparison with a standard instrument, such errors for one calorimeter amounting to nearly 2 per cent.

Examination of a very large amount of data obtained during the investigation indicates that with those calorimeters free from significant constant errors, total heating values should be determinable, under conditions obtaining in the industrial testing of gas, to an accuracy of the order of 1 per cent.

The methods of operation which this and other investigations have shown to be suitable for the various calorimeters are given in Bureau of Standards Circular No. 48 on Standard Methods of Gas

Testing in the form of detailed operating directions. The circular also contains other matters of interest in connection with the equipment of a calorimetric laboratory, as well as tables to be used in connection with heating value determinations.

The authors desire to express their appreciation of the assistance rendered by their colleagues throughout the investigation, among whom especial thanks are due to Messrs. H. C. Dickinson, D. R. Harper 3d, R. S. McBride, E. R. Weaver, and H. G. Barrott.

WASHINGTON, March 1, 1914.