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The heat of formation of water

Frederick D. Rossini

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Abstract

The usually accepted value for the heat of formation of water is based upon measurements made by Thomsen in 1873, Schuller and Wartha in 1877, and Mixter in 1903.The most reliable of these data are those of Schuller and Wartha, whose average value has an uncertainty of some 8 parts in 10,000, practically all of which lies in the calibration factor of their calorimeter.The procedure employed in the present investigation was to determine directly the quantitative correspondence between the energy liberated by (1) the reaction of hydrogen and oxygen to form a weighed mass of liquid H 2 and (2) a measured quantity of electrical energy, using the calorimeter as the absorber of the two quantities of energy and its temperature rise as the comparator.In so far as systematic errors are concerned, the absolute accuracy of the result obtained by this substitution method depends principally upon the determina- tion of the mass of water formed, in grams, and of the quantity of electrical energy, in terms of the mean solar second and the international volt and inter- national ohm as maintained at this bureau.High precision was obtained by the use of proper calorimetric technic, a sensitive device for measuring changes of temperature, a sensitive potentiometric system for measuring the electrical power input, a precise timing device, and a suitable balance for weighing the H2O formed.The data of two sets, each including the results of nine experiments, give for the heat of formation of liquid H 2 0, at 25 C. and a constant pressure of 1 atmosphere, 285,775 international joules per mole (18.0156 g).The estimated uncertainty in this value is 40 joules.With the factors 1.0004 and ^jog > this value is equivalent to 285,890 absolute joules and to 68,313 g cali5 -The maximum and the average deviations of the experiments, in per cent, are, respectively, 0.031 and 0.019 in Set I; 0.024 and 0.010 in Set II.The data of Schuller and Wartha, Thomsen, and Mixter, recomputed in terms of the international joule, are in substantial agreement with the value obtained in the present investigation.

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THE HEAT OF FORMATION OF WATER

By Frederick D. Rossini

ABSTRACT

The usually accepted value for the heat of formation of water is based upon measurements made by Thomsen in 1873, Schuller and Wartha in 1877, and Mixter in 1903. The most reliable of these data are those of Schuller and Wartha, whose average value has an uncertainty of some 8 parts in 10,000, practically all of which lies in the calibration factor of their calorimeter.

The procedure employed in the present investigation was to determine directly the quantitative correspondence between the energy liberated by (1) the reaction of hydrogen and oxygen to form a weighed mass of liquid H_2O and (2) a measured quantity of electrical energy, using the calorimeter as the absorber of the two quantities of energy and its temperature rise as the comparator. In so far as systematic errors are concerned, the absolute accuracy of the result obtained by this substitution method depends principally upon the determination of the mass of water formed, in grams, and of the quantity of electrical energy, in terms of the mean solar second and the international volt and international ohm as maintained at this bureau. High precision was obtained by the use of proper calorimetric technic, a sensitive device for measuring changes of temperature, a sensitive potentiometric system for measuring the electrical power input, a precise timing device, and a suitable balance for weighing the H_2O formed.

The data of two sets, each including the results of nine experiments, give for the heat of formation of liquid H_2O, at 25° C. and a constant pressure of 1 atmosphere, 285,775 international joules per mole (18.0156 g). The estimated uncertainty in this value is ± 40 joules. With the factors 1.0004 and $\frac{1.0004}{4.185}$, this value is equivalent to 285,890 absolute joules and to 68,313 g cal_{15}. The maximum and the average deviations of the experiments, in per cent, are, respectively, 0.031 and 0.019 in Set I; 0.024 and 0.010 in Set II.

The data of Schuller and Wartha, Thomsen, and Mixter, recomputed in terms of the international joule, are in substantial agreement with the value obtained in the present investigation.

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I. INTRODUCTION

The heat of formation of water is one of the most important constants in thermochemistry because it is involved directly in the calculation of the heats of formation of practically all organic and of many inorganic compounds.

The thermal energy liberated when hydrogen and oxygen gases combine to form water has been measured by many investigators. Of the 14 papers dealing with this problem during the past century, the first appeared in 1828 and the last in 1907.[1] The various experiments were performed under widely different conditions. Some involved combustion by explosion in a bomb at constant volume, while others were made by burning one of the gases in an atmosphere of the other at constant pressure. The reaction temperatures employed by the different investigators ranged from 0° C. to room temperature. The errors of measurement were much less for the investigators who worked after about 1860 than for their predecessors, because of the development of better measuring devices and technic. However, even in the case of the most reliable of these experiments, those of Schuller and Wartha in 1877, an uncertainty of about 8 parts in 10,000 still exists.[2]

With the great increase in accuracy and precision of calorimetric measuring instruments, methods, and devices, and with the facilities available for calibration and standardization at this bureau, it was felt that the uncertainty in the value selected for the heat of formation of water could be reduced to 1 or 2 parts in 10,000.

II. METHOD

The method employed in this investigation was as follows: The apparatus consisted of a calorimeter surrounded by a constant temperature jacket. The calorimeter was composed of a calorimeter can containing a weighed mass of water, a device for measuring changes of temperature, a stirring mechanism, a reaction vessel for burning the gases at constant pressure, and a heating coil. The problem was to determine the quantitative correspondence between the thermal energy liberated by (1) the reaction of hydrogen and oxygen to form a weighed mass of liquid H_2O, and (2) a measured quantity of electrical energy, using the calorimeter as the absorber of the two quantities of energy and its temperature rise as the comparator. A combustion experiment, in which a mass of m grams of water was formed in the reaction vessel, produced a temperature rise of Δt degrees in

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[1] These papers, as compiled by F. R. Bichowsky in the International Critical Tables, **5**, pages 176, 207–211, are listed in chronological order:
(*a*) Despretz, Annales de chimie et de physique, **37**, p. 180; 1828.
(*b*) Dulong, Comptes rendus, **7**, p. 871; 1838.
(*c*) Grassi, Journal de pharmacie et de chimie, **8**, p. 170; 1845.
(*d*) Abria, Comptes rendus, **22**, p. 372; 1846.
(*e*) Favre and Silbermann, Comptes rendus, **23**, p. 411; 1846.
(*f*) Andrews, Philosophical Magazine, **32**, p. 321; 1848.
(*g*) Thomsen, Annalen der Physik und Chemie, **148**, p. 368; 1873.
(*h*) von Than, Berichte, **10**, p. 947; 1877.
(*i*) Schuller and Wertha, Annalen der Physik und Chemie, **2**, p. 359; 1877.
(*j*) von Than, Annalen der Physik und Chemie, **13**, p. 84; 1881.
(*k*) Berthelot, Annales de chimie et de physique, **23**, p. 176; 1881.
(*l*) Berthelot and Matignon, Annales de chimie et de physique, **30**, 547; 1893.
(*m*) Mixter, Am. J. of Sci., **16**, p. 214; 1903.
(*n*) Rumelin, Zeitschrift für physikalische Chemie, **58**, p. 449; 1907.
The data obtained are reviewed in Section XII of this paper.

[2] The source of this uncertainty is explained in Section XII, p. 28 of this paper.

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the calorimeter at some average temperature t_1. In a calibration experiment, the same temperature rise of Δt degrees, at the same average temperature t_1, was brought about in the same calorimeter by a measured quantity of electrical energy, E joules. In this manner, the formation of m grams of water was found to be equivalent, in energy involved, to E joules of electrical energy.

In this substitution method many of the systematic errors of the calorimetry itself are eliminated, since they tend, in general, to affect both kinds of experiments similarly, and systematic errors in the value found for the heat of formation of water are to be expected to originate principally in the determination of the mass of H_2O formed and of the quantity of electrical energy. Accurate standards of mass

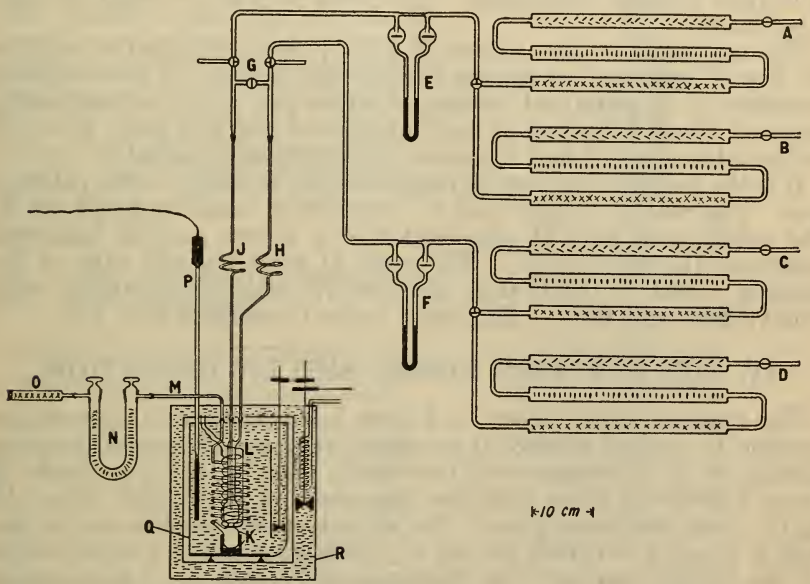


FIGURE 1.—*Schematic diagram of the apparatus*

A, B, C, D, purifying tubes; *E, F*, flow meters; *G*, stopcocks; *J, H*, inlet tubes; *K*, reaction vessel and support; *L*, calorimeter heater; *M*, connecting tube; *N*, U-tube absorber; *O*, guard tube; *P*, platinum thermometer; *Q*, calorimeter can; *R*, jacket.

and of the ohm, the volt, and the second were available at this bureau. High precision was obtained by the use of proper calorimetric technic, a platinum resistance thermometer with a sensitive galvanometric system for measuring changes of temperature, a sensitive potentiometric system for measuring the electrical power input, a precise timing device, and a suitable balance for determining the mass of H_2O formed.

III. APPARATUS ASSEMBLY

The assembly of the apparatus, exclusive of the measuring instruments, is shown to scale in Figure 1. All the parts through which the hydrogen and oxygen gases travel are made of Pyrex laboratory glass.

A, B, C, and *D* are each the entrance to a set of three purifying tubes which contain in order (1) "ascarite" (a sodium hydroxide-

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asbestos mixture) for removing CO_2 and other acidic oxides, (2) "dehydrite" ($Mg(ClO_4)_2.3H_2O$) for removing water vapor, and (3) P_2O_5 for removing the last traces of water vapor. For the experiments in which hydrogen was burned in oxygen, *A* and *C* were attached, respectively, to the cylinders of pure compressed hydrogen and oxygen used in the combustion, and *D* was connected to an extra cylinder of oxygen. This second cylinder of oxygen was used to flush out the system and to vaporize the H_2O collected as liquid in the condensing chamber of the reaction vessel so that it would be absorbed in the weighed tube *N*. For the experiments in which oxygen was burned in hydrogen, the connections to *A* and *C* were reversed, and to *D* was connected an extra cylinder of hydrogen replacing the extra cylinder of oxygen already mentioned. The train *B* was not used in these experiments.

The two mercury flow meters, *E* and *F*, were calibrated to indicate the flow of hydrogen or oxygen in liters per minute. The two 3-way stopcocks at *G* permitted wasting of either gas, while the connecting stopcock allowed flushing of both inlet tubes with one gas. The coils on the inlet tubes, *J* and *H*, served to permit easy assembly.

L is the heating coil used to impart electrical energy to the calorimeter. The reaction vessel with its supporting frame is shown at *K*. The calorimeter can, *Q*, also contained a stirrer and the platinum resistance thermometer *P*. The tube *M* joins the exit tube of the reaction vessel to the U-tube absorber *N*, which was charged with "dehydrite" and P_2O_5. The guard tube *O* was filled with P_2O_5.

IV. THE REACTION VESSEL AND ITS OPERATION

The reaction vessel, shown in Figure 2, was designed to permit the reaction to proceed quietly at constant pressure with one of the gases burning in an atmosphere of the other. This vessel was made of Pyrex laboratory glass with the exception of the burner tube, the tip of which was silica glass. The silica-to-pyrex graded seal on this tube is about 5 cm from the tip *F*. The glass vessel was supported by the brass frame *J*. The platinum wire leads at *A* were sealed through the two inlet tubes, *B* and *C*, and continued down into the inlet tubes of the reaction vessel where the continuity was broken by a gap of about 2 mm. Two other pieces of platinum wire, coiled at the top to assure rigidity in the tubes, extended down into the reaction chamber, one outside and one inside the burner tube.

The spark which ignited the gas issuing from the burner tube jumped across the gap at the tip *F*. The flame, some 5 mm long, burned quietly at *F* in the reaction chamber *G*. The H_2O formed as a vapor in *G* condensed and collected as a liquid in the condensing chamber below. The excess gas, plus a small amount of H_2O vapor, passed from the condensing chamber at *H*, through the cooling coil *E*, and out through the exit *D*.

In an actual combustion experiment the entire reaction vessel was first flushed out and filled with the excess gas, which in some experiments was oxygen and in others hydrogen. When, for example, the entire reaction vessel had been filled with hydrogen flowing at the desired rate, and the rate of flow of the oxygen, flowing through its waste tube (*G*, fig. 1) had been adjusted properly, the oxygen was switched into the tube *B*. One or two seconds later the spark-coil

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switch was closed, and the spark was permitted to jump across the gap at *F* for a measured number of seconds, two to six. This ignited the oxygen and the flame burned quietly in an atmosphere of hydrogen. The amount of hydrogen gas and water vapor issuing from the condensing chamber at *H* could be made to approach zero by reducing the amount of hydrogen gas to the stoichiometrical quantity required for its reaction with oxygen.

The platinum wires which formed part of the spark-coil circuit were made discontinuous at their entrance into the reaction vessel in order that the heat flow between the calorimeter system and its surroundings would be the same in the combustion experiments as in the calibration experiments with electrical heating where the reaction chamber remained cold.

V. THE CHEMICAL PROCEDURE

1. THE HYDROGEN AND OXYGEN

The amount of reaction in each combustion experiment was determined from the mass of H_2O formed, not from the mass of the H_2 or the O_2 consumed. It was, therefore, necessary only to obtain supplies of hydrogen and oxygen which contained no reactive gases other than O_2 or H_2. The presence of inert and nonreactive gases would not influence the experiments, either chemically or calorimetrically. This being the case, an examination of the reaction products would give definite and complete evidence as to the purity of the reaction.

Both the hydrogen and oxygen were regular commercial products obtained in steel cylinders. The former was of electrolytic and the latter of atmospheric origin. Analysis of the hydrogen and of the oxygen, after the gases had been passed through the purifying train shown in Figure 1, was made by the gas chemistry section of this bureau, in an improved gas analysis apparatus described in another paper.[3]

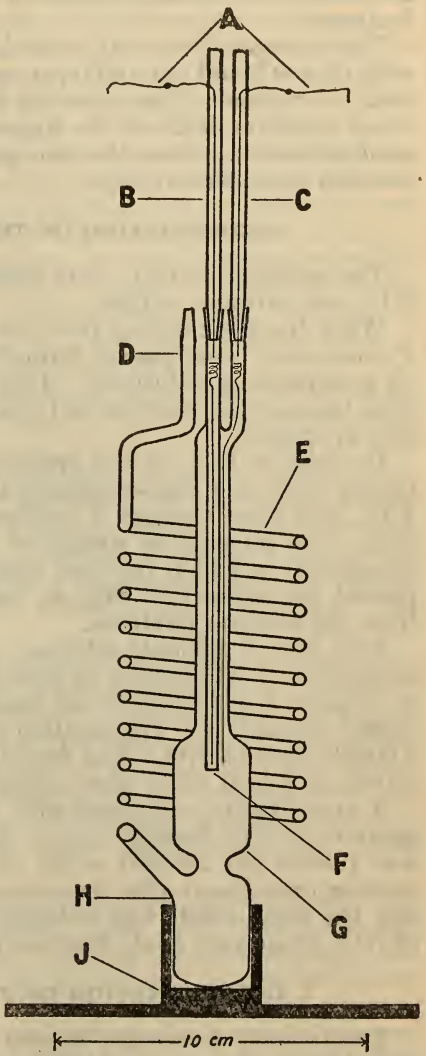


FIGURE 2.—*Cross section of the reaction vessel and supporting frame*

A, leads of spark circuit; *B*, *C*, inlet tubes; *D*, exit tube; *E*, cooling coil; *F*, burner tube; *G*, reaction chamber; *H*, condensing chamber; *J*, supporting frame.

[3] G. M. Shepherd, B. S. Jour. Research, **6** (RP266), p. 121; 1931.

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The amount of inert gas in the oxygen was found, in two analyses, to be 0.63 and 0.52 per cent. This inert gas was about two-thirds nitrogen and one-third argon plus neon. The presence of the rare gases in the oxygen offered no difficulty, but the N_2 might lead to the formation of a small amount of NH_3 when oxygen was burned in hydrogen.

The amount of impurity in the hydrogen which was noncombustible with O_2 was found to be 0.06 per cent in one determination and 0.09 per cent in another. This impurity was probably O_2. The presence of small amounts of O_2 in the hydrogen (or of H_2 in the oxygen) was unobjectionable, since the two gases were brought together in the reaction chamber anyway.

2. EXAMINATION OF THE REACTION PRODUCTS

The reaction products were examined for the presence of CO_2, SO_2, NH_3, and nitrogen oxides.

When the gases issuing from the reaction chamber during and after a combustion were passed through a saturated solution of $Ba(OH)_2$, no precipitate was formed. This test excluded the presence of CO_2 from the reaction products and of any carbon compound in the oxygen and hydrogen.

In order to test for the presence of SO_2, the exit gases were first passed through a glass-stoppered U-tube containing "dehydrite" and P_2O_5, and then through a weighed tube containing "ascarite" and P_2O_5. No increase in weight of the second tube was found in an experiment in which the first tube absorbed 6 g of H_2O. This test proved the absence of SO_2, as well as CO_2 and other acidic oxides, from the reaction products.

Acid ferrous sulphate solution, of the composition[4] best suited for absorption of NO or NO_2 to form the dark brown $Fe(NO)^{++}$, showed no change in color when the gaseous products of combustion were passed through it. The solution as used would have detected about 0.00003 mole of NO. The formation of this amount of NO would introduce a heat effect amounting to about 1 part in 20,000.

A quantitative color test with Nessler's reagent showed that the amount of NH_3 formed during the burning of oxygen in hydrogen was 1 mole per 250,000 moles of H_2O. This test was repeated in another experiment after vaporizing all the H_2O from the condenser, and the same result was obtained. The formation of this amount of NH_3 produces a heat effect amounting to about 1 part in 300,000.

3. DETERMINATION OF THE MASS OF H_2O FORMED

The amount of reaction in each combustion experiment was determined from the mass of H_2O formed. In each experiment, $m_{(H_2O)}$, the mass of H_2O formed, was equal to $m_1+m_2+m_3$. Here m_1 was the H_2O remaining as liquid in the condensing chamber, m_2 was the H_2O in the vapor phase within the reaction vessel, and m_3 was the H_2O carried as a vapor by the excess gas into the absorber (N, fig. 1) during the combustion period.

[4] Mellor, Treatise on Inorganic and Theoretical Chemistry, 8, p. 424, Longmans, Green & Co., New York; 1928.

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The average amount of H_2O formed in a combustion experiment was about 2.85 g, practically all liquid. m_3 was equal to the increase in weight of the absorber during the time of the combustion. At the completion of the calorimetric observations dry gas (oxygen when hydrogen was burned in oxygen, and hydrogen when oxygen was burned in hydrogen), at a rate of about 0.5 liter per minute, was passed through the reaction vessel. It was found by experiment that even with rates of flow up to 0.9 liter per minute, and with the gas completely saturated with water vapor, the U-tube absorbed all the H_2O within ± 0.1 mg. In about 6 to 12 hours, all the H_2O which had been in the reaction vessel, either as a liquid or as a vapor, was carried out into the absorber *N*. This second increase in weight gave m_1+m_2. The amount of H_2O not condensed to liquid during a combustion was m_2+m_3. The magnitude of m_3 depended on the amount of excess gas and could be made to approach zero by reducing the proportion of the excess gas to the stoichiometrical amount. The magnitudes of the three masses were usually as follows: m_1, 2.85 g; m_2, 0.0012 g (at 26.5° C.) or 0.0016 g (at 31.5° C.); and m_3, 0.007 to 0.020 g. m_3 was in one case purposely made as large as 0.077 g.

The U-tube absorber (*N*, fig. 1) was made of soft glass with ground glass stoppers and ground ends. When in use, the U-tube stoppers and all the other joints in the gas train were lubricated with a "general" lubricant [5] made in the gas chemistry section of this bureau. The U-tube (*N*, fig. 1) was 16 cm long and 6 cm wide, with a cross section of about 1.8 cm^2 and an internal volume of about 60 cm^3. For use in the absorption of H_2O, this tube was freshly filled with "dehydrite" and with a 2 cm layer of P_2O_5 at the exit end. Layers of clean, dry, acid-washed asbestos bounded the "dehydrite" and the P_2O_5.

The apparent increase in mass of the absorber after it had received all the H_2O formed in a given experiment was corrected to vacuum in order to obtain the true mass of the H_2O. This correction to vacuum required a knowledge of the increase in volume of the "dehydrite" upon the absorption of a given amount of H_2O. When $Mg(ClO_4)_2.3H_2O$ absorbs H_2O to form $Mg(ClO_4)_2.6H_2O$, the increase in volume is 0.60 cm^3 per gram of H_2O absorbed. This was calculated from the following densities, in grams per cm^3: $Mg(ClO_4)_2.3H_2O$, 2.044; $Mg(ClO_4)_2.6H_2O$, 1.970.[6]

The correction to vacuum was made as follows: After the absorber was properly charged with "dehydrite" and P_2O_5, lubricated, and thoroughly flushed out with the gas which was to be in excess in the combustion experiment to follow, the U-tube and its counterbalance were placed in the balance case. With one U-tube as the absorber and a second U-tube, equal in external volume, for a counterbalance, changes in the density of the air in the balance case would affect only the buoyancy on the brass weights. The counterpoise was closed and contained a fixed mass of air in all the weighings.

In order to produce equilibrium of the beams of the balance, *m* grams of brass weights were added to the right pan. Omitting the masses of the U-tubes, whose air buoyancies cancel, the initial balance was:

$$m_{(s)}+m_{(g)}=m-m_{(air)} \qquad (1)$$

[5] Shepherd and Ledig, Ind. Eng. Chem., **19**, p. 1059; 1927.
[6] International Critical Tables, **1**, p. 141.

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where $m_{(s)}$ was the mass of the solid matter in the absorber, $m_{(g)}$ was the mass of the gas in the absorber, m was the mass of the brass weights, and $m_{(air)}$ the mass of the air displaced by the brass weights.

After all the H_2O formed was taken up in the U-tube absorber, a new balance was made:

$$m'_{(s)} + m'_{(g)} = m' - m'_{(air)} \tag{2}$$

Here $m'_{(s)}$ was the mass of the solid matter now in the absorber. Since the volume of the solid in the absorber had increased, there was a numerically equal decrease in the volume of the gas in the absorber. The mass of the gas was now $m'_{(g)}$ while m' was the new mass of the brass weights, and $m'_{(air)}$ was the mass of the air displaced by these brass weights. $m'_{(s)}$ was equal to $m_{(s)}$ plus $m_{(H_2O)}$, the true mass of the H_2O absorbed. One may then write

$$m_{(s)} + m_{(H_2O)} + m'_{(g)} = m' - m'_{(air)} \tag{3}$$

Subtracting equation (1) from (3),

$$m_{(H_2O)} = (m' - m) + (m_{(g)} - m'_{(g)}) - (m'_{(air)} - m_{(air)}) \tag{4}$$

$m' - m$, or Δm, was the apparent increase in mass of the absorber and was less than $m_{(H_2O)}$ by about 7 parts in 10,000 with oxygen in the absorber and was greater than $m_{(H_2O)}$ by about 1 part in 10,000 with hydrogen in the absorber. $m_{(g)} - m'_{(g)}$ was the mass of that volume of gas in the absorber which had been displaced by the increase in volume of the solid. $m'_{(air)} - m_{(air)}$ was the mass of that volume of air occupied by the brass weights of mass, Δm. With the density of the air in the balance case equal to 0.0012 g per cm^3, and that of the brass weights equal to 8.4 g per cm^3, $m'_{(air)} - m_{(air)}$ was equal to 0.00014 g for $\Delta m = 1$. With oxygen in the U-tube absorber at 25° C. and 1 atmosphere, and for $\Delta m = 1$,

$$m_{(g)} - m'_{(g)} = 0.60 \times 0.00131 = 0.00079 \text{ g} \tag{5}$$

With hydrogen in the absorber

$$m_{(g)} - m'_{(g)} = 0.60 \times 0.000082 = 0.00005 \text{ g} \tag{6}$$

For the experiments in which oxygen was the excess gas

$$m_{(H_2O)} = (1 + 0.00079 - 0.00014) \times \Delta m = 1.00065 \Delta m \tag{7}$$

With hydrogen as the excess gas

$$m_{(H_2O)} = (1 + 0.00005 - 0.00014) \times \Delta m = 0.99991 \Delta m \tag{8}$$

In order to check this method of determining the true mass of H_2O, extra weighings were made in some experiments with each gas in the absorber both before and after the absorption. In this manner, $m_{(H_2O)}$ with oxygen in the absorber agreed with the value of $m_{(H_2O)}$ with hydrogen within 1 to 7 parts per 100,000. The accuracy of the correction to vacuum, while ample in both cases, is much more

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certain with hydrogen in the absorber because its density is only one-sixteenth that of oxygen.

In the actual experiments in which oxygen filled the absorber, the change in the density of the oxygen in the absorber between weighings was corrected for by calculation from the changes in its temperature and pressure. The mass of oxygen in the charged absorber was approximately equal to 16/15 times the decrease in weight of the absorber when the oxygen was replaced with hydrogen. Since the mass of the oxygen was usually 0.065 g, the total correction due to the change in the density of the oxygen in the absorber was −0.00022 g per degree increase in temperature at about 25° C. and 0.000086 g/mm increase in pressure at a pressure of about 1 atmosphere. The corresponding corrections for hydrogen were one-sixteenth of these values. This correction is independent of the amount of H_2O absorbed.

Many blank experiments were made by passing oxygen or hydrogen through the entire system connected as shown in Figure 1. The observed changes in mass of the absorber in these blank experiments were always zero within 0.1 to 0.2 mg. In order to obtain blanks of this order, great care was needed in the manipulation and handling of the U-tube and none but properly lubricated ground-glass joints were used throughout the gas train. Only the stoppers of the U-tube were touched by hand, while the U-tube proper was handled in clean bleached cheesecloth. The lubricant on the connecting joints of the U-tube was carefully removed with ether before each weighing. In weighing, uniformity of procedure was employed in order that unknown constant errors, if any existed, would cancel. The balance employed was located in the same room close to the calorimeter and was, therefore, at all times subjected to the same constant atmospheric conditions as was the absorption tube. For this reason and the fact that the absorber was not touched by hand, the time for establishment of equilibrium in the balance case was about 20 minutes. Accordingly, all weighings were made 20 minutes after the absorber was placed in the balance case. The entire system, as well as the absorber, was thoroughly flushed out before each experiment.

The weights used were calibrated against the mass standards of this bureau by the mass section. The ratio of the arms of the balance used in these weighings was $\frac{L}{R}=1.000007$. The weighings were made to the nearest 0.05 mg.

VI. CALORIMETRIC APPARATUS AND MEASURING INSTRUMENTS

1. THE CALORIMETER AND THE THERMOMETRIC SYSTEM

A schematic cross section of the calorimeter, which with some minor changes was the one used in this laboratory [7] to determine the heat of formation of SO_2, is given in Figure 1. R is the constant-temperature water jacket with its heater and stirrer. A 20-junction thermel (thermoelement) used for reading the variations in the temperature of the jacket water, is not shown. Q is the calorimeter can containing its stirrer, K is the reaction vessel and supporting frame, P, the platinum resistance thermometer, and L, the heating

[7] Eckman and Rossini, B. S. Jour. Research, 3, p. 597; 1929.

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coil. The air space between the calorimeter can and the jacket was about 1 cm. The calorimeter can was supported on three ivory cones and contained about 3,700 g of distilled water.

The platinum thermometer was immersed to the same marked depth in all the calorimetric experiments. A counted number of drops of oil, usually six, was placed on the surface of the water in the calorimeter can at the openings in order to reduce evaporation. The three openings in the cover of the calorimeter can, which coincided with holes in the jacket cover, served to permit the passage of (1) the platinum resistance thermometer P, (2) the connecting tubes, J, H, and M, to the reaction vessel, and (3) the leads to the heating coil.

A special room, of dimensions 10 by 10 by 30 feet, was used to house all the apparatus. With the window, door, and ventilating openings closed, the temperature of this room changed not more than 0.1° or 0.2° C. per hour, and it was thus possible to maintain the temperature of the jacket water constant simply by passing a steady current through the jacket heater. This current was regulated manually as need required.

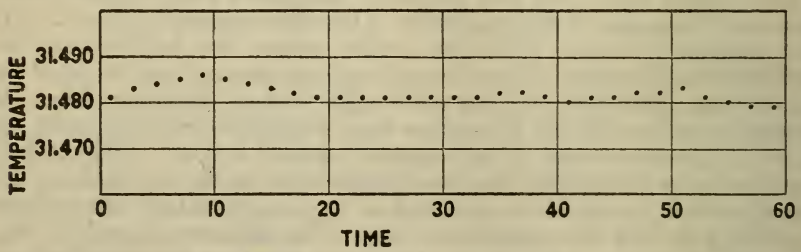


FIGURE 3.—*A plot showing the variation of the jacket temperature with time*

The ordinate scale gives the temperature in °C. while the abscissa scale marks the time in minutes. The data are from experiment S–AA.

In Figure 3, the jacket temperature (data from combustion experiment S–AA) is plotted against the time. The jacket temperature was read every two minutes by means of the 20-junction copper-constantan thermel and, at the conclusion of each experiment the thermel was compared directly with the platinum resistance thermometer. The data illustrated in Figure 3 show that the temperature of the jacket changed very little in the course of a run and these changes were known at each instant to 0.001° C.

In all of the calorimetric experiments, the temperature of the calorimeter can and contents was below that of the jacket, and the rate of heat transfer from the latter to the former was such as to increase the temperature of the calorimeter can and contents about 0.002° C. per minute per °C. difference in temperature.

The speed of stirring of the calorimeter water, which varied not more than 1 or 2 per cent over the time of each experiment, ranged from 200 to 240 r. p. m. The energy contributed by this stirring was about 4 joules per minute for a speed of 200 r. p. m.

The platinum resistance thermometer and bridge had been used in a previous investigation in this laboratory.[8] The constants of the

[8] See footnote 7, p. 9.

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thermometer then were: $R_0 = 25.6230$ international ohms; $R_{100} - R_0 = 10.0136$ international ohms; $\delta = 1.487$. R_0 was again measured by the thermometry section of this bureau, and found to be 25.6233 international ohms.

The transfer values used for $\frac{dR}{dt}$ and $\frac{d^2R}{dt^2}$ are:

	25° C.	30° C.	
$\frac{dR}{dt}$	0. 100880	0. 100731	ohm/° C.
$\frac{d^2R}{dt^2}$	−. 000030	−. 000030	ohm/° C./° C.

The method of converting an increase in resistance of the platinum thermometer into a temperature rise in degrees is described in previous papers,[9] [10] but such conversion is, of course, not necessary and is made for psychological purposes only.

The resistance of the platinum thermometer was read on a Mueller thermometer bridge (Leeds & Northrup No. 47669). A high powered telescope, placed about 1 m from the galvanometer, was focused on the galvanometer mirror which reflected a highly illuminated scale placed in a box mounted on the wall opposite the galvanometer, some 8 m distant. The sensitivity of the galvanometer was such that a change of 0.0001 ohm was equivalent to a change of 5.2 mm on the galvanometer scale, so that, approximately, 1 mm was equivalent to 0.0002° C. Readings on the galvanometer scale could be estimated to 0.1 mm.

The coils of the thermometer bridge were not kept in a thermostat. This fact did not militate greatly against the precision obtained in the calorimetric experiments because (1) the temperature of the room was not more than 2° to 3° C. different in the various calibration and combustion experiments of a given set and (2) the variation of the room temperature during an experiment was but 0.1° or 0.2° C. per hour. The temperature coefficient of resistance of the 0.1 ohm coils of the measuring bridge was about 10 parts per million per degree increase in room temperature. In two experiments made at constant room temperatures which differed by 1° C., the error on conversion of the increase in thermometer resistance into ° C. would be 1 part in 100,000. The possibility of error arising from the second factor listed above is much greater, but this source of error was eliminated by the manner of recording the data. The gradual change in the room temperature would change the reading of the thermometer even though its resistance were constant, but as 20-minute observation periods were made before and after the 20-minute reaction period, the gradual changes in resistance of the coils in the thermometer bridge due to the gradual and uniform change in room temperature became incorporated as part of the drift in the "fore" and "after" periods. The completeness of the elimination of this error depends upon the constancy of the rate of change of the room temperature during the time of the observations.

The resistance coils in the thermometer bridge were calibrated by the resistance measurements section of this bureau.

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[9] Dickinson and Mueller, B. S. Bull. 9, p. 483; 1913.
[10] See footnote 7, p. 9.

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The temperature of the jacket was determined with a 20-junction copper-constantan thermel, with one leg at 0° C. in a vacuum flask containing ice and water and the other in the well-stirred jacket water. The e. m. f. of the thermel was read every two minutes on a White double potentiometer (Leeds & Northrup No. 156585). The thermel was calibrated against the platinum thermometer so that small changes of e. m. f. could be converted into ohms. This factor was 80 micro volts per 0.01 ohm. At the conclusion of each experiment the platinum thermometer was placed in the water jacket, and the thermel was compared directly with it.

2. THE ELECTRICAL ENERGY SYSTEM

The heating coil, shown as L in Figure 1, was made by drawing down thin copper tubing over double silk covered No. 36 B. and S. gage constantan wire which had previously been covered with a thin coating of bakelite. The resistance wire was insulated throughout from the copper tube inclosing it. The leads to the resistance coil were No. 24 B. and S. gage enameled copper wire. A 1-inch piece of thin ⅛-inch copper tubing, insulated from the wire, was placed over the region where the copper leads were soldered to the resistance wire. In this manner the circuit for the heating current was completely insulated from the calorimeter water and can.

The copper leads were brought up through an opening at the edge of the cover of the calorimeter can, and after crossing the 1 cm air space were cemented firmly with de Khotinsky wax to the calorimeter jacket. No. 28 B. and S. gage copper leads, for measuring the voltage drop across the heating coil, were soldered to the current leads midway between their point of contact with the calorimeter water and the jacket. All the leads were in good thermal contact with, but electrically insulated from, the calorimeter water and the jacket. Actually, the point at which the potential leads were attached to the current leads was slightly closer to the jacket than to the calorimeter water. The potential readings were corrected for this small difference, a displacement of 1 mm being equivalent to about 2 parts per 1,000,000 of the reading.

The electrical energy input into the calorimeter was determined by measuring (1) the potential drop across the heating coil and (2) the potential drop across a standard resistance through which passed the same current (less a small calculable amount which flowed through the potential coils in parallel with the heating coil). These voltages were measured on a White double potentiometer having a range of 100,000 microvolts. The sensitivity of these measurements was such that 1 mm on the galvanometer scale (1 m distant from the galvanometer) was approximately equivalent to 2 microvolts. The scale readings were estimated to 0.1 mm.

The energy-measurement circuit is shown in Figure 4. At A are the leads from a storage battery of 70 volts. B designates the external stabilizing resistance, equal to the resistance of the calorimeter heater. C represents the calorimeter heater. The potential drop across the standard 0.1 ohm resistance at D was measured on the potentiometer at H. E and F are standard resistances of 10,000 and 10 ohms, respectively. The potential drop across F was measured on the potentiometer at G.

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In this manner the current through the calorimeter heating coil C is given by $\frac{1}{r_D}\left(1-\frac{r_C}{r_E+r_F}\right)e_H$, the potential measured at H. The potential drop across the heating coil C is equal to $\frac{r_E+r_F}{r_F}e_G$, the voltage measured at G. The readings of e_H, which serve as a measure, of the current through the calorimeter, are shown in the upper part of Figure 5; while the readings of e_G, which measure the voltage drop across the heating coil, are plotted in the lower part. These data are the actual readings taken in experiment S–2. Readings of e_H and e_G were made, respectively, on the P and Q dials of the potentiometer within 10 or 15 seconds of each other on the half minute. The operator then was free to take the platinum theremometer readings on the even minute.

As can be seen from the data plotted in Figure 5, the variation of the current and voltage is small enough so that the energy input can be calculated as the product of the time, the average current, and the average voltage. The difference between this simple method of deter-

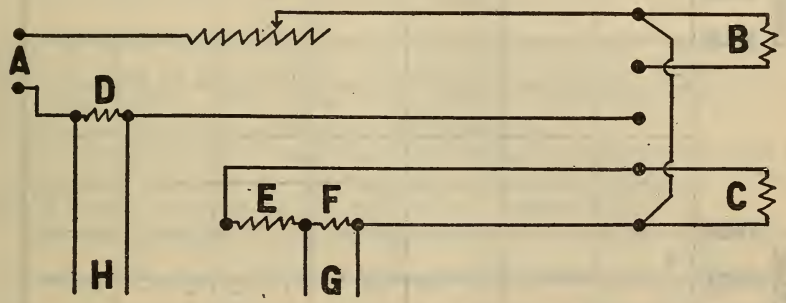


FIGURE 4.—*Diagram of the electrical energy circuit*

A, 70-volt storage battery; *B*, external stabilizing resistance; *C*, calorimeter heater; *D*, *E*, *F*, standard resistances of 0.1, 10,000, and 10 ohms, respectively; *G*, *H*, leads to potentiometer.

mining the energy input, and the more exact but laborious method of integrating the watts input, is not greater than 1 or 2 parts per 1,000,000, for any of the energy data taken.

The standard cell used with the potentiometer to measure E_H and E_G was compared, both before and after the experiments were performed, with the standard cells of this bureau, while the resistances D, E, and F, and the resistance coils of the potentiometer, were similarly compared with those of this bureau. The accuracy of these standardizations was certified to 1 part in 20,000 for r_D and r_F, to 1 in 10,000 for r_E, to 1 in 50,000 for the standard cell, and to 1 in 10,000 for the potentiometer readings (when over 20,000 microvolts).

The time of the electrical energy input was 11 to 13 minutes. In the first set of experiments this time interval was measured on a Gaertner chronograph having two pens recording on a revolving cylinder. The seconds impulses were transmitted to the chronograph from the master clock in the time section of this bureau. One of the two pens marked each second while the other pen was in circuit with one side of a special V-type quick acting double-pole double-throw knife switch whose other side was part of the electrical energy circuit.

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The throwing of this switch simultaneously sent energy into the calorimeter and recorded the time on the chronograph paper. The alignment of the two knife-edges of the switch with their respective clip receptacles was checked, and in several blank time experiments, the two sides of the switch recorded the same time within 0.02 second. The cylinder was 15 cm in diameter and revolved at such a rate that a point on its periphery moved about 16 mm per second. It is estimated that the accuracy of this device in measuring a time interval of 12 minutes is about 1 part in 20,000.

For the second set of experiments a new timing device was obtained. This timing device is the same as that of Johnston,[11] with some im-

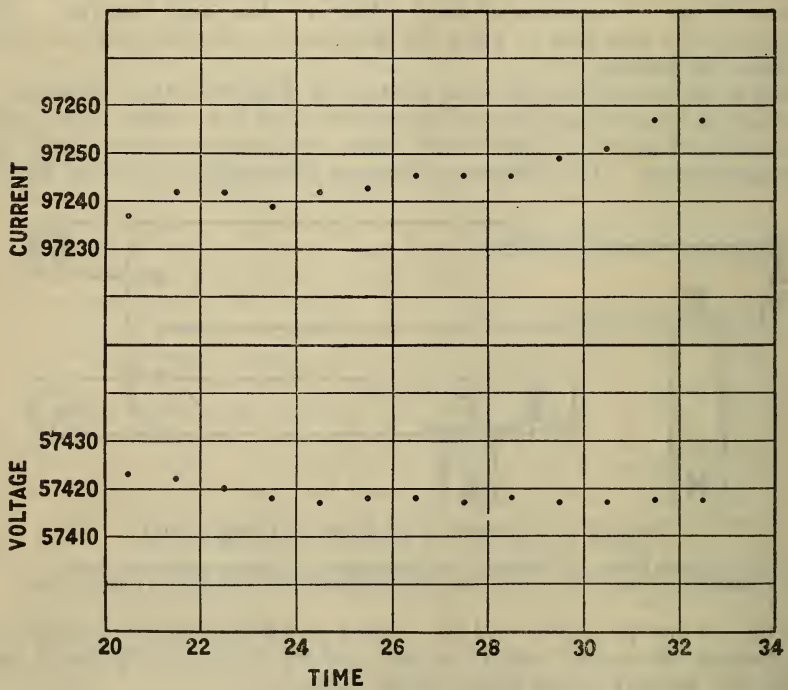


FIGURE 5.—*Plot showing the variation of the current readings and of the voltage readings with time*

The ordinate scale measures the actual potentiometer readings in microvolts, while the abscissa scale gives the time in minutes.

provements suggested by him. The principal improvement consists of a device for preventing the main sprocket wheel (marked *W* in the descriptive sketch)[11] from rotating more than one notch per impulse. This is accomplished by having two sprocket wheels, firmly joined to each other, one of which receives the impulses from the shaft *B* while the other is equipped with a back stop to prevent rotation of more than one notch.[12]

Measured with this timing device, the time of the electrical energy input (about 700 seconds) is estimated to be accurate to 1 part in 100,000.

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[11] Johnston, J. Opt. Soc. Am. and Rev. Sci. Inst., **17**, p. 381; 1928.
[12] This timing device was built by G. F. Nelson, Berkeley, Calif.

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VII. MOLECULAR WEIGHTS, CONSTANTS, UNITS, FACTORS

The atomic weights of oxygen and hydrogen were taken as 16.000 and 1.0078, respectively. [13]

The unit of electrical energy used in this investigation is the international joule and is that defined by (1) the international ohm as maintained at this bureau by standard resistance coils, (2) the international volt as maintained at this bureau by standard cells, and (3) the mean solar second.[14]

The factor 1.0004 is used to convert international into absolute joules.[15]

In order to correct the slightly varying amounts of water in the calorimeter can to a common mass, the heat capacity of water was taken as 4.175 and 4.173 international joules per gram at 25° and 30° C., respectively. To correct the heat capacity of the water to a common average temperature, the temperature coefficient was taken as −0.00050 and −0.00027 joule per gram per degree per degree at 25° and 30° C., respectively.[16]

For the reaction

$$H_{2(gas)} + \tfrac{1}{2}O_{2(gas)} = H_2O_{(liquid)} \qquad (9)$$

ΔC_p at 25° C. is calculated to be 32 joules per mole [16]; that is, Q, the heat evolved in the reaction, decreases 32 joules per degree increase in temperature. This value was used in correcting values of the heat of formation to a common temperature.

In calculating the "vaporization" energy corrections to the heat of reaction, the heat of vaporization of water was taken as 2,439 and 2,428 joules per gram at 25° and 30° C., respectively.[17]

For the purpose of converting the data of other investigators, 1 g-cal.$_{15}$ is taken equal to 4.185 absolute joules, or $\frac{4.185}{1.0004}$ international joules, and the heat capacity of water at various temperatures is calculated from the Callendar formula: [18]

$$c = 0.98410 + \frac{0.504}{t+20} + 0.0084\ \frac{t}{100} + 0.009\left(\frac{t}{100}\right)^2 \qquad (10)$$

In this formula, t is in °C., and c gives the heat capacity in g-cal.$_{15}$

[13] Baxter, 1930 Report of the Committee on Atomic Weights, J. Am. Chem. Soc., 52, p. 861; 1930.

[14] Standards of the international ohm and the international volt are similarly maintained in the other national laboratories of the world. On the basis of intercomparisons reported during the last five years, the international joule derived from the standards so maintained by the various countries differs from that in the United States by the amounts shown in the following table:

Country	Difference
	Per cent
Germany	−0.013
Great Britain	+.001
France	−.009 (?)
Japan	+.003
United Socialist Soviet Republics	−.012

This information is furnished by the electrical division of this bureau.

[15] This conversion factor is that recommended in the Technical New Bulletin of the Bureau of Standards, No. 156; April, 1930.

[16] International Critical Tables, 5, pp. 78, 80, and 82.

[17] Osborne, Stimson and Fiock, B. S. Jour. Research, 5, p. 479; 1930

[18] Callendar, Trans. Royal Soc. London (A) 212, p. 1; 1912.

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VIII. THE PRELIMINARY AND CORRECTION EXPERIMENTS

1. CALORIMETRIC PROCEDURE

In all the calorimetric experiments at 25° C., the jacket temperature was maintained constant at 26.5° C., and the initial and final temperatures of the calorimeter water were, respectively, 23.5° and 26.5° C. For the experiments at 30° C., the corresponding temperatures were 31.5° C. for the jacket and 28.5° and 31.5° C. for the calorimeter water.

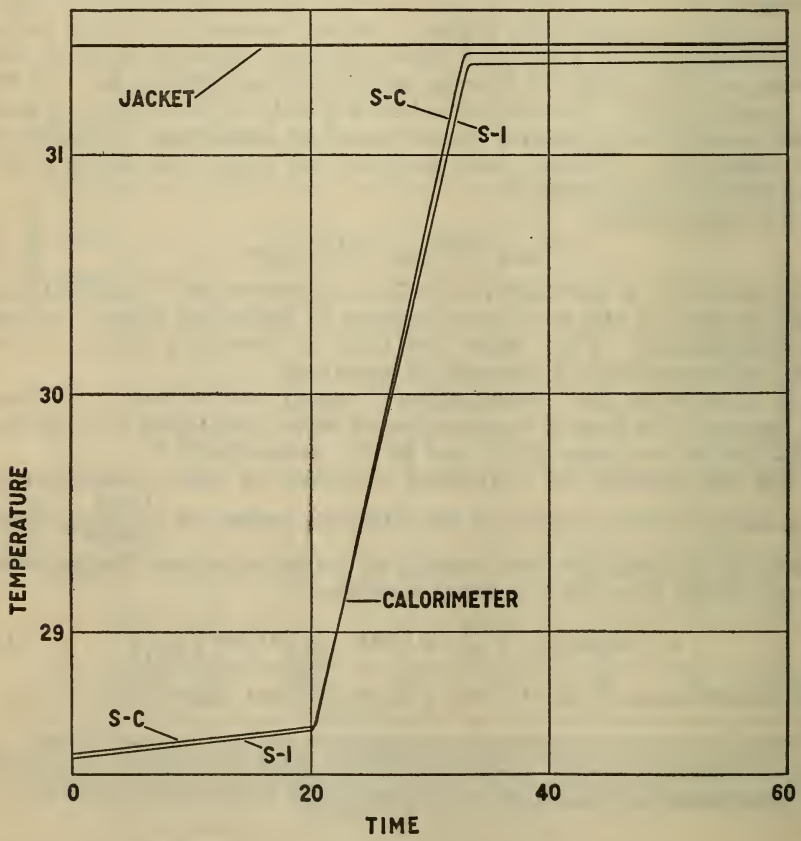


FIGURE 6.—*Plot showing the variation of the calorimeter temperature with time*

The ordinate scale gives the temperature in °C. and the abscissa scale marks the time in minutes. Curve *S–I* is for electrical calibration experiment *S–I*, and curve *S–C* is for combustion experiment S–C.

In each experiment the observations were divided into three periods. First, the "fore" period of 20 minutes in which readings of the calorimeter water and the jacket temperatures were made. Second, the "reaction" period of 20 minutes in which electrical energy or combustion energy was supplied to the calorimeter water at a rate which brought it to the final temperature in 12 or 13 minutes, leaving a time of 7 or 8 minutes for attainment of equilibrium in the calorime-

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ter system. In this period observations of the calorimeter water temperature were made every minute and of the jacket temperature every two minutes. For the calibration experiments readings of the current and voltage were made every minute. Third, the "after" period of 20 minutes in which readings of the temperature of the calorimeter water and of the jacket water were taken.

In Figure 6 are curves of the temperature of the calorimeter and of the jacket plotted against the time in minute. Curve *S*–1 represents the data of calibration experiment *S*–1 with electric heating, while curve *S*–*C* shows the data of combustion experiment *S*–*C*. These curves portray the substantial identity of the calorimetric conditions in the two kinds of experiments. With such a procedure, any unknown constant error in determining the true temperature rise is eliminated and does not affect the comparison of electrical with combustion energy.

The method of determining the true or corrected temperature rise, Δt, is explained in a previous paper.[19] In the text and the tables of the present paper, R represents the temperature reading of the calorimeter water expressed in ohms on the platinum thermometer; R_j is the jacket temperature reading converted into ohms on the platinum thermometer; Z is the time in minutes; a numerical subscript indicates the time in minutes at which the given observation was made; k is the proportionality factor, in ohms per minute per ohm, for the flow of heat energy from the jacket and surroundings to the calorimeter system; k measures, in ohms, the total amount of this temperature rise in the time from Z_{20} to Z_{40}, and is evaluated by multiplying k by the area, in Figure 6, which is bounded by the calorimeter and jacket lines and the ordinates at 20 and 40 minutes; u is the constant rate at which the calorimeter temperature increases (or decreases) and is chiefly due to the energy input of stirring and energy removal by evaporation; U measures, in ohms, the total amount of this temperature change in the time from Z_{20} to Z_{40}, and is equal to $(Z_{40}-Z_{20})\,u$ or $20\,u$.

From the observations taken in the "fore" period, one can write

$$u+\left(R_{j(0,\,20)}-\frac{R_0+R_{20}}{2}\right)k=\frac{R_{20}-R_0}{20} \tag{11}$$

The data of the "after" period give

$$u+\left(R_{j(40,\,60)}-\frac{R_{40}+R_{60}}{2}\right)k=\frac{R_{60}-R_{40}}{20} \tag{12}$$

These equations are solved for u and k in each experiment, whence U and K can be calculated as already indicated.

The main temperature rise of the calorimeter system is measured by

$$R_{40}-R_{20}=\Delta R \tag{13}$$

Then the corrected temperature rise is equivalent to

$$\Delta R-U-K=\Delta R_{\text{corr}} \tag{14}$$

and the true or corrected temperature rise in degrees is obtained by

[19] See footnote 7, p. 9.

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dividing ΔR_{corr} by the value of $\frac{dR}{dt}$ for the average temperature of the experiment.

$$\Delta t_{corr} = \frac{\Delta R_{corr}}{\frac{dR}{dt}} \tag{15}$$

The actual operations in a calibration experiment at 30° C. were:

(*a*) The current from the storage battery was switched to the external stabilizing resistance which had previously been made equal in resistance to the calorimeter heater.

(*b*) The temperature of the water in the calorimeter jacket was brought to 31.5° C. The current through the jacket heater was adjusted from time to time so that the jacket temperature remained constant.

(*c*) The clean, dry calorimeter can, with the supporting frame for the reaction vessel, was placed in position on the three ivory cones.

(*d*) The clean, dry reaction vessel, with the exit tube properly lubricated, was placed in the supporting frame.

(*e*) About 3,700 g of distilled water, whose temperature was about 27° C., was weighed to 0.01 g and carefully poured into the calorimeter can. This operation included weighing a clean beaker (with greased lip to facilitate pouring) before and after the water was poured from it. (Losses from evaporation in this operation were assumed to be the same for all experiments since a uniform procedure was employed. The actual loss by evaporation was found to be not more than 0.15 g, and the variability of this was negligible.)

(*f*) The tightly fitting cover of the calorimeter can was placed in position with its three openings properly aligned. Two drops of oil were added through each of the openings. The jacket cover was rotated into position. The platinum thermometer, the exit tube, and the two inlet tubes, properly lubricated, were placed in position. The stirring, both of the jacket and the calorimeter water, was begun.

(*g*) The temperature of the calorimeter water was brought up to 28.5° C. by means of the heating coil in the calorimeter water.

(*h*) Readings of the room temperature were made every 10 minutes.

(*i*) When equilibrium was established in the calorimeter system, observations were begun. Readings of the platinum thermometer and of the jacket thermel were made every two minutes in the "fore" period.

(*j*) At the twentieth minute, the timing device having been set, the current was switched into the calorimeter system and readings of the current, the voltage, and the platinum thermometer were taken every minute, while the jacket thermel was read about every two minutes. At the thirty-third minute the timing device switched the current back to the external stabilizing resistance.

(*k*) The "after" period ran from the fortieth to the sixtieth minute, and here observations of the platinum thermometer and jacket thermel readings were made every two minutes.

(*l*) The platinum thermometer was transferred from the calorimeter to the jacket water where the jacket thermel and platinum thermometer readings were taken simultaneously. The thermel

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reading, in microvolts, was thus converted directly into ohms on the resistance thermometer.

The operations in the combustion runs were the same except that operation (*a*) was omitted, (*j*) was changed, and several others were added, as follows:

(*aa*) The U-tube absorber was cleaned, properly charged, flushed out, and filled with hydrogen, weighed, and placed in position with its guard tube, after the calorimeter system was thoroughly flushed out and filled with hydrogen. The ends of the U tube were lubricated after the weighing.

(*bb*) The rates of flow of hydrogen and oxygen were adjusted. Here hydrogen was in excess.

(*j*) The hydrogen was turned on at the twentieth minute. The oxygen was then turned on, and about two seconds later the spark circuit was closed for a measured time of two to six seconds. The oxygen was now ignited and burning quietly. Readings of the calorimeter temperature were taken every minute and of the jacket temperature every two minutes. At the proper time, around the thirty-second minute, the oxygen and hydrogen were turned off to waste.

(*m*) The U-tube absorber, with its guard tube and exit tube, was removed and closely joined (with a rubber tube connection) to the hydrogen waste tube. The exit *D* (fig. 2) was stoppered. Thus the small amount of H_2O which condensed in the tube *M* (fig. 1), when the room temperature was below the jacket temperature, was carried into the U-tube absorber. The tube *M* was replaced and its exit end was stoppered. The lubricant was removed from the ends of the U tube, which was then weighed and replaced in the system. (Blank experiments on this operation were made to make sure that no H_2O was taken up from the rubber. Dry gas passing through the waste tube removed any moisture which may have condensed on the rubber tube when not used in this operation.)

(*n*) A flow of dry hydrogen, about 0.5 liter per minute, was now sent into the reaction vessel, through both inlet tubes. At the end of 6 to 12 hours, when all the H_2O in the reaction vessel had been vaporized and carried into the U-tube absorber, the U tube was removed, the ends were cleaned with ether, and the final weighing was made.

2. EVALUATION OF "SPARK," "GAS," "AND "VAPORIZATION" ENERGY

In the combustion experiments, there were three sources or sinks of energy, in addition to the heat of the given reaction, which were not present in the calibration experiments. These were (1) the energy given to the calorimeter by the spark which was used to start the combustion, (2) the energy taken up from the calorimeter by the oxygen and hydrogen entering the calorimeter at a temperature lower than the average temperature of the calorimeter, and (3) the energy of vaporization of the H_2O not condensed to liquid. The approximate magnitudes of these energy items were, respectively, 2, 2 to 8, and 5 to 25, parts per 10,000, of the total energy of the experiment.

The value of the "spark" energy was determined by passing the spark into the calorimeter when its temperature was slightly below

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that of the jacket. The time of sparking was made about ten times that employed in the combustion experiments. The resulting small temperature rise in the calorimeter measured the amount of this sparking energy. Two experiments were made, with the following results:

		I	II
Time of sparking	seconds	30	30
Energy	joules	54	56
Spark energy	joules/second	1. 80	1. 86
Average	do	1. 83	

The "gas" energy, which was that energy taken up by the inflowing gases entering at a temperature below the average temperature of the calorimeter, was calculated from the known heat capacity of the gases and the difference between their temperature (taken as that of the room) and the average temperature of the calorimeter. For this purpose the heat capacities of hydrogen and oxygen were taken as 28.6 and 29.2 joules per mole,[20] respectively.

The "vaporization" energy was that required to vaporize (1) the H_2O carried out of the calorimeter as a vapor by the excess gases and (2) the H_2O remaining in the reaction vessel as a vapor. The mass of the H_2O in (1) was determined by weighing the absorber before and after the combustion, as already described, and that in (2) was calculated from the known vapor pressure of water at 26.5° C. (and 31.5° C.) and the internal volume of the reaction vessel and tubes.

The internal volume was 51½ cm^3. From this was subtracted about 3 cm^3 occupied by the liquid H_2O formed. The mass of H_2O vapor in the reaction vessel at 26.5° and 31.5° C. was then 0.0012 and 0.0016 g, respectively. The heat of vaporization of H_2O was taken as 2,439 and 2,428 international joules per gram at 25° and 30° C., respectively.[21]

In several experiments, the "gas" energy and the "vaporization" energy were purposely made large in order to test the validity of the foregoing assumptions. In order to check collectively the corrections for "spark," "gas," and "vaporization" energy the following experiment was performed:

The calorimeter was brought to within 0.3° C. of the jacket temperature, which was 31.5° C. The "fore" period observations were taken in the usual manner. At the beginning of the "reaction" period, the combustion was started in the usual manner, but was stopped after a period of about 15 seconds. This was repeated twice. These three small combustions resulted in a temperature rise of the calorimeter due to the algebraic sum of (1) the heat of formation of the small amount of H_2O formed, (2) the "spark" energy, (3) the "gas" energy, and (4) the "vaporization" energy.

[20] International Critical Tables, 5, pp. 80 and 82.

[21] See footnote 17, p. 15.

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The following data were obtained in this experiment:

Electrical equivalent of calorimeter system	int. joules/°C	15712. 0
Corrected temperature rise	°C	. 18501
E: Total energy	int. joules	2896. 7
Spark time	seconds	15
E_2: "Spark" energy	joules	27. 5
Volume of inflowing gases	liters	1. 09
Temperature difference between room and colorimeter	°C	−7. 0
E_3: "Gas" energy	joules	−9. 0
Mass of H_2O carried out of colorimeter as vapor	g	. 0157
Mass of H_2O remaining in reaction vessel as vapor	do	. 0016
Total H_2O formed as vapor	do	. 0173
E_4: "Vaporization" energy	joules	−41. 9
Total amount of H_2O formed	g	. 18416
E_1: Heat of formation of the H_2O (285,580 int. joules/mole at 31° C.)	int. joules	2919. 2

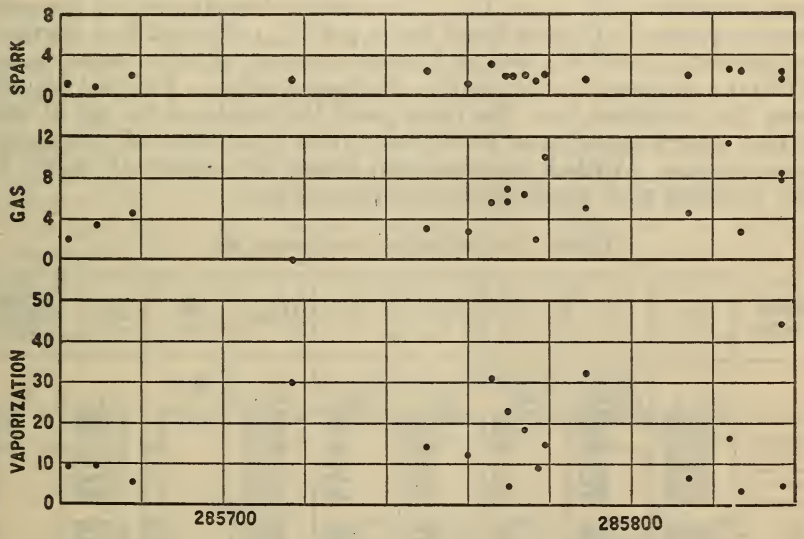


FIGURE 7.—*Plot showing the magnitude of the "vaporization," "gas," and "spark" energy relative to the total energy in each experiment, plotted against the heat of formation value obtained in that experiment*

The ordinates in each case are parts in 10,000 of the total energy while the abscissa give the values for the heat of formation in international joules per mole at 25° C. and 1 atmosphere.

The sum of the energies, $E_2+E_3+E_4+E_1$, should be equal to E, and a difference greater than the experimental error would indicate that the manner of determining E_2, or E_3, or E_4, is invalid, or that some unknown heat effects accompanied the ignition or the extinction of the flame.

$$E_2+E_3+E_4+E_1=2{,}895.8 \text{ int. joules} \qquad (16)$$

The difference of 0.9 joule between this figure and the value of E is within the experimental error.

In Figure 7 are plotted the values of the "spark," "gas," and "vaporization" energies, in parts per 10,000 of the total energy of a given experiment, against the value obtained for the heat of formation of H_2O in that experiment. This plot shows no trend in the

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value obtained for the heat of formation of H_2O with variations in the magnitude of the various energy corrections. In one experiment the "vaporization" energy was 40 times, and in another the "gas" energy was 10 times, the experimental error.

IX. THE EXPERIMENTS AT 25° C.

The first set of experiments was made at 25° C. with the room temperature around 20° to 23° C. These experiments were made between January 18, 1930, and March 1, 1930. The time of energy input on these experiments was measured with a chronograph as explained in Section V, 2, p. 13.

The results of the calibration experiments are shown in Table 1. The symbols heading each column have the significance attached to them in Section VIII, 1, p. 17. The electrical equivalent of the calorimeter system, in international joules per °C., corrected to a common temperature, 25.00° C., and to a common mass of calorimeter water, 3,700.00 g, is given in the next to the last column. The last column gives the deviation from the mean, and the result of the set of calibration experiments gives for the electrical equivalent of this calorimeter system, 15,725.9 international joules per degree at 25.00° C. with 3,700.00 g of water in the calorimeter can.

TABLE 1.—*Calibration experiments, Set I*

Experiment	ΔR	k	u	K	U	ΔR corr.	$\frac{dR}{dt}$	Δt corr.	Average temperature
	Ohm	*Ohms/min/ohm*	*Ohms/min*	*Ohm*	*Ohm*	*Ohm*	*Ohms/° C.*	*° C.*	*° C.*
1	0.283622	0.002053	0.0000200	0.003410	0.000400	0.279812	0.100876	2.77382	25.14
4	.270009	2052	288	4016	576	.265528	78	2.63217	.07
5	.273817	1968	246	3633	492	.269703	76	2.67361	.12
6	.274047	1945	65	3439	130	.270495	75	2.68149	.16
7	.274931	2034	−6	4153	−12	.270301	77	2.68447	.09
8	.291275	2008	151	3691	302	.287309	78	2.84808	.08
9	.284553	2040	133	3537	266	.280777	76	2.78338	.12
10	.283982	2020	322	3608	644	.279757	77	2.77325	.09
11	.292274	1843	113	3365	226	.288710	77	2.86200	.10
12	.287468	2035	105	3814	210	.283471	78	2.81004	.07
13	.290186	1989	190	3755	380	.286078	78	2.83588	.06

Experiment	e/r (current)	e (voltage)	Time	Electrical energy	Mass of calorimeter water	Electrical equivalent of calorimeter system	Correction to 25.00 ° C.	Correction to 3700.00 g water	Electrical equivalent of calorimeter system [1]	Deviation from mean
	Int. volts/int. ohms	*Int. volts*	*Mean solar seconds*	*Int. joules*	*g*	*Int. joules/° C.*	*Joules/° C.*	*Joules/° C.*	*Int. joules/° C.*	
1	0.939911	65.1998	716.06	43,831.6	3,721.35	15,819.9	0.26	−39.20	15,731.0	5.1
4	.920735	63.8906	704.79	41,460.2	3,705.97	15,751.3	.13	−24.94	26.5	0.6
5	.918639	63.7515	719.86	42,160.6	3,709.42	15,769.2	.22	−39.35	30.0	4.1
6	.937667	65.0632	689.95	42,092.2	3,694.18	15,697.3	.30	24.31	21.9	−4.0
7	.902491	62.6314	749.76	42,379.7	3,714.95	15,787.0	.17	−62.40	24.7	−1.2
8	.967220	67.1024	689.77	44,768.0	3,698.85	15,718.7	.15	4.81	23.6	−2.3
9	.976529	67.7423	660.36	42,717.4	3,695.41	15,706.6	.22	19.17	26.0	.1
10	.975881	67.6959	659.74	43,584.5	3,699.02	15,716.0	.17	4.10	20.3	−5.6
11	.976502	67.7414	674.56	44,621.9	3,667.69	15,591.2	.19	135.00	26.4	.7
12	.959378	66.5390	690.03	44,048.8	3,688.15	15,675.5	.13	49.50	25.2	−.5
13	.959811	66.5880	697.98	44,609.2	3,700.20	15,730.3	.11	−0.34	29.6	3.7
Mean									15,725.9	±2.5

[1] Corrected to 3,700.00 g of water and an average temperature of 25.00° C.

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In Table 2 are given the results of the combustion experiments at 25° C. The electrical equivalent, given in the thirteenth column, is obtained by correcting the value 15,725.9 international joules per °C. to the average temperature of the given experiment and to the given mass of water, and then adding to this the heat capacity of one-half the amount of liquid H_2O formed during the experiment. In this table the experiments labeled with a single letter are those in which hydrogen was burned in oxygen, while those having a double letter indicate that oxygen was burned in hydrogen.

The pressure correction to 1 atmosphere is calculated from the thermodynamic equation:

$$w = nRT \log_e \frac{P}{760} \qquad (17)$$

where w is the energy in joules to be added; n is taken as the number of moles decrease in gaseous volume; R is the gas constant in joules per degree; T is the absolute temperature; P is the reaction pressure in mm of Hg (mercury barometer readings are corrected to 0° C.). For values of P from 750 to 770 mm, w is calculated to be 5 joules per mole per mm increase in pressure. The pressure in the reaction chamber was determined by adding to the pressure in the room, the pressure drop between the reaction chamber and the final exit tube of the gas line. This latter pressure was determined in separate experiments, for various rates of flow, to be $\Delta P = aL$ where L is the total flow of gas in liters per minute and a is approximately equal to 10 mm /l/min. In most of the experiments, ΔP was 0.5 to 1.0 mm. The pressure in the reaction chamber is given to the nearest mm.

TABLE 2.—*Combustion experiments, Set I*

Experiment	ΔR	k	u	K	U	$\Delta R_{corr.}$	$\frac{dR}{dt}$	$\Delta t_{corr.}$
	Ohm	*Ohms/min/ohm*	*Ohms/min*	*Ohm*	*Ohm*	*Ohm*	*Ohms/° C.*	*° C.*
B	0.290281	0.001904	0.0000135	0.004002	0.000270	0.286009	0.100877	2.83523
C	.298530	2024	121	3153	240	.295135	77	2.92569
D	.295118	1912	65	3213	130	.291776	78	2.89237
E	.279496	2038	143	3685	286	.275525	76	2.73132
F	.281385	2019	−1	3622	−2	.277761	76	2.75349
G	.286564	2071	109	3740	218	.282606	77	2.80149
H	.293339	2045	39	3926	78	.289335	78	2.86817
CC	.293706	1877	266	3634	532	.289540	78	2.87020
DD	.295146	1919	114	3907	228	.291011	78	2.88478

Experiment	Average temperature	Mass of calorimeter water	One-half mass of liquid H_2O formed	Electrical equivalent of calorimeter system	Pressure in reaction chamber	Total energy	"Gas" energy	"Vaporization" energy
	° C.	*g*	*g*	*Int. joules/° C.*	*mm Hg*	*Int. joules*	*Joules*	*Joules*
B	25.10	3,694.65	1.40	15,709.2	754	44,539.2	−13.8	−60.7
C	.11	3,694.56	1.44	15,709.0	754	45,959.7	−10.0	−40.3
D	.07	3,712.03	1.43	15,782.0	762	45,647.4	−8.5	−41.1
E	.15	3,706.02	1.35	15,756.4	753	43,035.8	−14.6	−40.4
F	.14	3,700.88	1.34	15,734.7	766	43,325.3	−36.4	−191.2
G	.11	3,707.08	1.37	15,761.0	763	44,154.3	−22.6	−142.9
H	.08	3,696.04	1.41	15,715.1	761	45,073.6	−12.7	−54.3
CC	.08	3,696.59	1.42	15,717.4	752	45,112.1	−20.3	−22.4
DD	.08	3,689.50	1.42	15,689.1	763	45,259.6	−12.3	−17.3

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TABLE 2.—*Combustion experiments, Set I*—Continued

Experiment	"Spark" energy	Reaction energy	Quantity of H_2O formed	$Q_{t,p}$	Temperature correction to 25.00 °C.	Pressure correction to 1 atmosphere	$Q_{25°C.,\ 1\ atm.}$	Deviation from mean
	Joules	*Int. joules*	*Mole*	*Int. joules/mole*	*Joules/mole*	*Joules/mole*	*Int. joules/mole*	
B	11.0	44,602.7	0.156075	285,777	+3	−30	285,750	1
C	7.3	46,002.7	.160959	804	+3	−30	777	28
D	5.5	45,691.5	.159956	650	+2	10	662	−87
E	3.7	43,087.1	.150813	699	+5	−35	669	−80
F	9.2	43,543.7	.152356	802	+5	30	837	88
G	7.3	44,313.1	.155068	766	+3	15	784	35
H	5.5	45,135.1	.157952	752	+3	5	760	11
CC	9.2	45,145.6	.158009	715	+3	−40	678	−71
DD	11.0	45,278.2	.158421	809	+3	15	827	+78
Mean							285,749	±53

X. THE EXPERIMENTS AT 30° C.

It was planned originally to perform all the experiments at 25° C., but after the completion, on about March 1, 1930, of experiment DD, the combustion experiments which were then made gave results which indicated that the calorimetric apparatus was not functioning properly. The first two or three of these odd experiments gave values completely at variance with one another, and far beyond the limits of experimental error. Then three experiments gave concordant results, but were not in agreement with any previous values. Several not very satisfactory calibration experiments were made, and apparently the heat capacity of the calorimeter had changed slightly. During all of these latter experiments it was noted that the ivory supports for the calorimeter can had worn down considerably and unevenly, causing the stirring mechanism to rock the calorimeter can. At this time the calorimeter heater was broken.

About April 1, the calorimeter system was changed. New ivory supports replaced the worn ones. New belting was put in the stirring system. A new cover for the calorimeter can was made. The old heating coil for the calorimeter water was shortened and repaired, and its resistance was now 59.5 as against 69.4 ohms before. The new timing device, described in Section VI, 2, p.14, of this paper, was installed. The jacket temperature was made 31.5° C. and the experiments were conducted at 30° C. because the room temperature was now about 23° to 27° C. All the calibration and combustion experiments at 30° C. were completed in four weeks, beginning April 19, 1930.

The results of the calibration experiments in the new calorimeter system at 30° C. are given in Table 3. The letter S designates experiments of this second set. The agreement of the last four of the five calibration experiments is extraordinarily good. The increased precision in the electrical calibration experiments can be attributed in great part to the use of the new timing device. In calculating the mean of these experiments, the result of S–1 is given a weight of one-third.

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TABLE 3.—*Calibration experiments, Set II*

Experiment	ΔR	k	u	K	U	$\Delta R_{corr.}$	$\frac{dR}{dt}$
	Ohm	*Ohms/min/ohm*	*Ohms/min*	*Ohm*	*Ohm*	*Ohm*	*Ohms/° C.*
S-1	0.282183	0.001907	0.0000133	0.004024	0.000266	0.277893	0.100731
S-2	.281962	1927	48	4045	96	.277781	.100730
S-3	.291376	1959	−10	3953	−20	.287443	.100729
S-4	.283590	1926	−29	3995	−58	.279653	.100730
S-5	.291792	1830	−56	3612	−112	.288292	.100727

Experiment	$\Delta t_{corr.}$	Average temperature	e/r (current)	e (voltage)	Time	Electrical energy
	° *C.*		*Int. volts / Int. ohms*	*Int. volts*	*Mean solar seconds*	*Int. joules*
S-1	2.75876	30.01	0.966970	57.5296	780.000	43,390.9
S-2	2.75768	.02	.966781	57.4735	780.000	43,340.2
S-3	2.85363	.08	.982747	58.4275	780.000	44,787.1
S-4	2.77626	.02	.969952	57.6717	780.000	43,632.3
S-5	2.86211	.13	.985700	58.6627	780.000	45,102.6

Experiment	Mass of calorimeter water	Electrical equivalent of calorimeter system [1]	Correction to 30.00° C.	Correction to 3,700.0 g. water	Electrical equivalent of calorimeter system [1]	Deviation from mean
	g.	*Int. joules/° C.*	*Joules/° C.*	*Joules/° C.*	*Int. joules/° C.*	
S-1	3,702.93	15,728.4	0.01	−12.24	15,716.2	4.7
S-2	3,698.71	15,716.2	.02	5.39	21.6	.7
S-3	3,693.47	15,694.8	.08	27.26	22.2	1.3
S-4	3,699.00	15,716.2	.02	4.18	20.4	−.5
S-5	3,709.04	15,758.5	.13	−37.73	20.9	−.0
Mean [2]					15,720.9	±1.0

[1] Corrected to 3,700.00 g of water and an average temperature of 30.00° C.
[2] The result of experiment S-1 has been given a weight of one-third.

The data of the combustion experiments at 30° C. are given in Table 4. Each value is corrected to 25° C. so that comparison can be made with the results of the first set. The temperature and pressure corrections are made as previously explained.

TABLE 4.—*Combustion experiments, Set II*

Experiment	ΔR	k	u	K	U	ΔR_{corr}	$\frac{dR}{dt}$	Δt_{corr}
	Ohms	*Ohms/min/ohm*	*Ohms/min*	*Ohm*	*Ohm*	*Ohm*	*Ohms/° C.*	° *C.*
S-A	0.288111	0.001790	−0.0000123	0.003763	−0.000204	0.284552	0.100729	2.82493
S-B	.295429	1821	−121	3118	−242	.292553	29	2.90436
S-D	.288904	1854	142	3534	284	.285086	29	2.83022
S-E	.283402	1876	3	3553	6	.279843	29	2.77818
S-BB	.287493	1892	244	4155	488	.282850	30	2.80800
S-CC	.281811	1882	81	3997	162	.277652	29	2.75643
S-DD	.284101	1913	111	3834	222	.280045	29	2.78018
S-EE	.294760	1866	156	3557	312	.290891	29	2.88786
S-FF	.287014	1873	12	4117	240	.28273	29	2.80826

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TABLE 4.—*Combustion experiments, Set II*—Continued

Experiment	Average temperature	Mass of calorimeter water	One-half mass of liquid H_2O formed	Electrical equivalent of calorimeter system	Pressure in reaction chamber	Total energy	"Gas" energy	"Vaporization" energy
	° C.	g	g	Int. joules/° C.	mm Hg	Int. joules	Joules	Joules
S-A	30.08	3,701.08	1.39	15,731.1	759	44,439.3	−50.7	−70.9
S-B	.07	3,719.05	1.43	15,806.4	763	45,907.5	−46.6	−66.2
S-D	.05	3,693.07	1.40	15,697.8	762	44,428.2	−36.5	−19.1
S-E	.07	3,695.00	1.37	15,705.7	759	43,633.3	−30.1	−19.1
S-BB	.04	3,686.90	1.37	15,671.9	757	44,006.7	−25.3	−99.2
S-CC	.07	3,697.97	1.34	15,617.9	755	43,325.3	−19.9	−133.3
S-DD	.07	3,685.36	1.35	15,665.3	754	43,552.4	1.3	−129.8
S-EE	.07	3,689.40	1.43	15,682.5	759	45,288.9	−20.4	−28.4
S-FF	.05	3,694.37	1.38	15,703.1	760	44,098.4	−28.3	−79.9

Experiment	"Spark" energy	Reaction energy	Quantity of H_2O formed	$Q_{p,t}$	Temperature correction to 25.00° C.	Pressure correction to 1 atm.	$Q_{25^\circ C}$ 1 atm.	Deviation from mean
	Joules	Int. joules	Mole	Int. joules/mole	Joules/mole	Joules/mole	Int. joules/mole	
S-A	11.0	44,549.9	0.155952	285,664	163	−5	285,822	41
S-B	9.2	46,011.1	.161103	600	162	15	777	−4
S-D	9.2	44,474.6	.155688	664	162	10	833	52
S-E	9.2	43,673.3	.152911	612	162	−5	768	−13
S-BB	9.2	44,122.0	.154477	621	161	−15	769	−12
S-CC	9.2	43,469.3	.152190	625	162	−25	762	−19
S-DD	7.3	43,673.6	.152929	581	162	−30	713	−68
S-EE	9.2	45,328.5	.158682	656	162	−5	813	32
S-FF	9.2	44,197.4	.154748	610	162	0	772	−9
Mean							285,781	±28

XI. SUMMARY AND DISCUSSION OF THE RESULTS

In order to compare the results of the experiments of Set I with those of Set II, and later to compare the results of the recomputed data of other investigators, the precision measure used in this paper will be the "95.45% error." This is

$$\text{"error" of the mean} = \pm 2\sqrt{\frac{\Sigma(\bar{x}-x)^2}{n(n-1)}} \qquad (18)$$

where $\Sigma(\bar{x}-x)^2$, is the sum of the squares of the deviations of n experiments. On the ordinary probability theory, the chance that the true average will lie within the above range is 95.45 in 100. The percentage errors of the calibration and combustion experiments in each set are combined by taking the square root of the sum of the squares. In this way, the data of Table 5 are obtained:

TABLE 5

		Number of experiments	"Error"	Combined "error"	Average value	"Error"	"Best" value	"Error"
			Per cent	Per cent				
Set I	Calibration	11	0.013	0.021	285,749	±60	285,775	±34
	Combustion	9	.016					
Set II	Calibration	5	.007	.010	285,781	±28		
	Combustion	9	.008					

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The "best" value with its "error" is obtained by weighting the two average values inversely as the squares of their assigned "errors."

An examination of the results also gives the following information:

	Value	Deviation from "best" value
Mean, Set I	285,749	−28
Median, Set I	285,760	−17
Mean, Set II	285,781	+6
Median, Set II	285,772	−3
"Best" value	285,775	0

There are several points in connection with the combustion experiments which affect the results to a negligible extent but which should be mentioned here. The first of these is the fact that a small amount of Hg vapor is carried into the region of reaction by the gases flowing through the flow meters. The amount of Hg carried into this region is calculated to be not more than 0.0000006 mole Hg in each experiment.

The second point to consider is the possible formation of H_2O_2 in the experiments in which hydrogen was burned in oxygen. If any H_2O_2 were formed in these experiments, all but a negligible amount must have decomposed into H_2O and O_2 in the reaction vessel because no pronounced differences were found in the results of the two kinds of experiments.[22]

Another point to consider is the fact that the liquid H_2O formed was saturated with O_2 in some experiments and with H_2 in the others. Following a calculation similar to one described by Washburn[23] we find that the heat effect of this saturation with O_2 is about 0.05 joule per mole of H_2O formed, or 1 part in 5,000,000. The effect of saturation with H_2 is of the same order of magnitude.

Still another question to consider is whether the excess gas leaves the calorimeter at the calorimeter temperature. Since the amount of excess gas can be made to approach zero, the error in this regard can also be made negligible. However, since in those experiments in which a large excess of gas was deliberately made to flow through the calorimeter no measurably different results were obtained, the temperature of the exit gases must have been very near to that of the calorimeter.

XII. THE WORK OF PREVIOUS INVESTIGATORS

The reported investigations on the heat of formation of water which have appeared in the past century are listed in Section I, p. 2, of this paper. These data have been critically reviewed by Lewis,[24] by Roth,[25] and by Bichowsky.[26]

Of all the experiments on the heat of formation of water, only those of Schuller and Wartha [27] have attached to them a high measure of

[22] This conclusion is substantiated by the recent work of Riesenfeld and Wassmuth, Zeitschrift für Physikalische Chemie, **149**, p. 140; 1930.
[23] Washburn, Sci. **61**, p. 55; 1925.
[24] Lewis, J. Am. Chem. Soc., **28**, p. 1389; 1906.
[25] Roth, Zeitschrift für Electrochemie, **20**, p. 228; 1920.
[26] This review is unpublished, but the result obtained appears in the International Critical Tables, **5**, p. 176.
[27] See footnote 1 (*i*), p. 2.

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reliability and precision. Schuller and Wartha burned oxygen in hydrogen at constant pressure in a glass reaction vessel in an ice calorimeter at such a rate that a mass of about 1.3g of H_2O was formed in three and one-half to four hours. The diminution of volume due to the melting of ice in the calorimeter can (determined from the weight of mercury taken up) served as a measure of the energy evolved. The mass of H_2O formed in the reaction was determined by weighing the reaction vessel before and after the combustion. No significant corrections because of the H_2O formed as a vapor were necessary because of the low vapor pressure of H_2O at 0°C. and because practically a zero amount of excess gas was used in the combustion.

In order to calibrate their calorimeter system in terms of some reproducible unit of energy, Schuller and Wartha dropped a weighed amount of water in a weighed glass container from a steam bath into the ice calorimeter at 0° C. Since the vapor space in the glass container was made negligible, according to Schuller and Wartha, by sealing the vessel at 100° C., these experiments gave the calibration factor in terms of the mean calorie.

The calibration data of Schuller and Wartha are given in Table 6. In this table the original data are italicized, and the other numbers are the writer's recalculations of the data. The results of these five calibration experiments show that 0.015442 g Hg was equivalent to 1 mean calorie.

TABLE 6.—*Calibration experiments of Schuller and Wartha*

Mass of glass container =0.19158 g
Mass of water in container = *.72530* g (in vacuo)

Experiment	Temperature	Grams Hg	Grams Hg corrected to 100° C.	Grams [1] Hg corrected for glass container	Deviation from mean
	° C.				
1	*99.65*	*1.1747*	*1.1788*	1.1208	0.00076
2	*.70*	*40.*	*75*	195	−54
3	*.60*	*47*	*94*	214	136
4	*.95*	*60*	*71*	191	−94
5	*.90*	*62*	*74*	194	−64
Mean				1.12004	±0.00085

[1] It was found that 1 g of the same kind of glass dropped from a steam bath into the ice calorimeter was equivalent to *0.30284* g Hg. The container is therefore equivalent to *0.0580* g Hg.

Osborne, Stimson, and Fiock [28] have determined the relation between the mean calorie, defined as one-one hundredth of the difference in heat content of liquid H_2O, under its own vapor pressure, between 0° and 100° C., and the international joule derived from standards maintained at this bureau. They found that 4.1875 international joules are equivalent to 1 mean calorie. The calibration figures of Schuller and Wartha can now be recalculated in terms of this unit of energy and, as a result,

$$0.0036877 \text{ g Hg} \sim 1 \text{ international joule} \qquad (19)$$

The data of the combustion experiments of Schuller and Wartha are given in Table 7. They report in their paper that certain irreg-

[28] See footnote 17, p. 15.

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ularities, unnamed, were present during the course of experiment 3, and they do not use this value in computing their average. Following their advice, the result of experiment 3 is excluded from the present average of their results. This gives the value 285,890 international joules per mole at 25° C. and a constant pressure of 1 atm.

Combining the "error" (as defined in the preceding section, equation (17)), of their calibration experiments with that of the combustion experiments, by taking the square root of the sum of the squares of the percentage "errors," there results for the heat of formation of 1 mole of liquid H_2O (18.0156 g) at 25° C. and 1 atm., from the measurements of Schuller and Wartha, 285,890 ± 235 international joules.

Schuller and Wartha do not mention the magnitude of the "spark" energy used in starting their combustions. A correction for "spark" energy would lower their average value by 15 joules per mole for each joule of spark energy.

TABLE 7.—*Combustion experiments of Schuller and Wartha*

Experiment	Mass of H_2O	Mass of Hg	Pressure in reaction chamber	Total energy	Mole of H_2O	Reaction energy per mole at 0° C., P	Pressure correction to 1 atmosphere	Temperature correction to 25° C.	$Q_{25°C.,1atm}$	Deviation from mean
	g	*g*	*mm Hg*	*Int. joules*		*Int. joules/mole*	*Joules/mole*	*Joules/mole*	*Int. joules/mole*	
1	*1.27008*	*74.5310*	*762*	20,210.7	0.070499	286,681	10	−800	285,890	0
2	*1.39350*	*81.7368*	*772*	22,164.9	.077350	553	60	−800	285,810	−80
3	*1.39022*	*81.6133*	*776*	22,131.2	.077168	792	80	−800	(286,070)	------
4	*1.38082*	*81.0227*	*771*	21,971.1	.076646	657	55	−800	285,910	+20
5	*1.38348*	*81.1946*	*765*	22,017.7	.076793	715	25	−800	285,940	+50
Mean									285,890	±38

The next best existing data on the heat of formation of water are those of Thomsen [29] and of Mixter.[30] Thomsen burned oxygen in hydrogen at constant pressure in a platinum reaction vessel in a calorimeter whose temperature rise was about 4° C. at an average temperature of 18° C. The amount of H_2O formed was determined by weighing the reaction vessel before and after the combustion. The amount of water vapor carried out of the calorimeter by the excess hydrogen was also determined. The temperature rise was measured with a mercury thermometer.

Thomsen calculated the heat capacity of the calorimeter can, reaction vessel, etc., to be 60 calories in terms of the 18° calorie as the unit of energy. The calorimeter contained 2,400 g of water whose average temperature during the experiment was 18° C. As nearly as one can judge from the few details given by Thomsen, the reaction vessel must have been saturated with water vapor before and after each combustion, so that no correction for vaporization of the amount of H_2O vapor required to fill the vessel was necessary. However, a small correction for the amount of H_2O which would vaporize as the temperature of the 500 cm^3 vessel rose from 16° to 20° C. was not made by Thomsen. At the start of the first and second experiments, the amount of H_2O in the platinum reaction vessel was negligible for the purpose of computing the total heat capacity, but

[29] See footnote 1 (*g*), p. 2. [30] See footnote 1 (*n*), p. 2.

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at the start of the third experiment there were 4 g of water in the reaction vessel.

The second and third experiments of Thomsen each really consisted of three separate experiments at 18° C., but the amount of H_2O formed was determined only for each group of three, so that only one value results from each group.

The data of Thomsen are given in Table 8, where the original data are italicized. Thomsen makes no mention of the amount of energy in the spark used to ignite the oxygen, nor of the pressure in the reaction chamber. The temperature of the inflowing gases was approximately equal to the average temperature of the calorimeter. The factor 4.1801 is used to convert 18° calories to international joules.[31]

TABLE 8.—*Combustion experiments of Thomsen*

Experiment	Heat capacity of calorimeter system	One-half heat capacity of H_2O formed	Total heat capacity	Corrected temperature rise	Total energy	Mass of H_2O formed	Mole of H_2O	Mass of H_2O carried out of reaction vessel as vapor
	g-cal. $_{18}$/° *C.*	*g-cal.* $_{18}$/° *C.*	*Int. joules/° C.*	*° C.*	*Int. joules*	*g*		*g*
1	*2,460*	1.1	10,288	*3.383*	33,765	*2.129*	0.11818	*0.020*
2	*2,460*	4.0	10,300	*12.321*	126,907	*7.989*	.44345	*.066*
3	*2,464*	4.4	10,318	*13.508*	139,376	*8.810*	.48902	*.089*

TABLE 8.—*Combustion experiments of Thomsen*

Experiment	Mass of H_2O formed as vapor in reaction vessel	"Vaporization" energy	Reaction energy	$Q_{18°\,C.}$	Correction to 25° C.	$Q_{25°\,C.}$	Deviation from mean.
	g	*Joules*	*Int. joules*	*Int. joules/mole*	*Joules/mole*	*Int. joules/mole*	
1	0.0018	53	33,818	286,157	−224	285,930	110
2	.0054	174	127,081	286,573	−224	286,350	530
3	.0054	230	139,606	285,481	−224	285,260	−560
Mean						285,820	±480

The three results are weighted according to the amount of water formed, and the mean value for the heat of formation of liquid H_2O at 25° C. becomes, from Thomsen's data, 285,820 ± 700 international joules per mole. The error assigned to this value includes an estimated "error" in calibration of 0.10 per cent which in this case comes in the determination of the water equivalent of the calorimeter can, stirrer, reaction vessel, thermometer, etc.

Mixter determined the heat of combustion of hydrogen by exploding the gases in a bomb at constant volume. The heat capacity of the calorimeter system was calculated from that of the parts. The amount of reaction was determined by calculating the mass of hydrogen from its volume, temperature, and pressure. The bomb, whose internal volume was 1,110 cm^3, was filled with hydrogen at 1 atmosphere and oxygen at slightly more than one-half atmosphere.

[31] See Section VII, p. 15.

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The data of the 14 experiments performed by Mixter are given in Table 9. The original data are italicized. The heat capacity of the calorimeter parts is calculated from the masses of Cu, Ag, Zn, and Ni, as reported by Mixter, and the heat capacity values given for these substances at 16° to 18° C. in the International Critical Tables.[32] The value given in this table is about 3 joules larger than that calculated by Mixter. One-half the heat capacity of the water formed is used in calculating the total heat capacity of the system, since the average temperature is taken as the temperature of the reaction. The values taken for the heat capacity of water, in international joules per gram, are:[33] 15° C., 4.1834; 16° C., 4.1822; 17° C., 4.1811; 18° C., 4.1801. The mass of H_2O formed as vapor is calculated from the known vapor pressure of H_2O and the final temperature of the calorimeter and the internal volume of the bomb. The values used for the heat of vaporization of water are, in international joules per gram:[34] 2,461 at 15° C. and 2,450 at 20° C. The number of moles of H_2O formed is determined from the molecular weight 2.0156 and the mass of H_2 as calculated by Mixter.

The measured reaction energy at constant volume is corrected (1) from constant volume and the average temperature to constant volume at 17° C., (2) from constant volume at 17° C. to a constant pressure of 1 atm. at 17° C., and (3) to a constant pressure of 1 atm. at 25° C. The first correction is made by taking the temperature coefficient of the heat evolved in the reaction at constant volume as -44 joules per mole per ° C. The second correction is made from the thermodynamic relation, $H=E+PV$, where H is the molal heat content, E is the molal internal energy, V is the molal volume, and P is the pressure. The third correction is made by taking the temperature coefficient[35] of the heat evolved in the reaction at constant pressure as -32 joules per mole per ° C.

In computing the average value from these data, all the experiments of Series I are excluded because of the extremely large deviations in this group. The assigned error for the average value, $285{,}760 \pm 600$ international joules per mole at 25° C., 1 atm., includes an estimated "error" in calibration of 0.10 per cent which arises from the evaluation of the heat capacity of the calorimeter system. Both Mixter, and Roth[36] who recalculated the data of Mixter, included the results of Series I in obtaining their average. After one combustion experiment, Mixter tested for the presence of silver and found about 1 mg. This was due to the formation of silver nitrate from the silver bomb and the nitrogen and oxygen. If an amount of silver nitrate corresponding to 1 mg of silver was formed in all his experiments, then the average value of Mixter as given above should be decreased about 20 joules.

Of the experiments on this problem by other investigators, the results obtained by the early experimenters served admirably well in their day, but are now only landmarks on the road to greater precision and accuracy in these measurements. This group of investigators[37] includes Andrews, Favre and Silbermann, Abria, Grassi, Dulong, and Despretz.

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[32] International Critical Tables, 5, pp. 85, 86, and 93.
[33] See Section VII, p. 15.
[34] See footnote 17, p. 15.
[35] See footnote 16, p. 15.
[36] See footnote 25, p. 27.
[37] See footnote 1, p. 2.

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TABLE 9.—*Combustion experiments of Mixter*

Experiment	Mass of water in calorimeter	Heat capacity of calorimeter water at average temperature	Heat capacity of H_2O formed	Total heat capacity at average temperature [1]	Average temperature of experiment	Corrected temperature rise	Energy	Mass of H_2O formed as vapor	"Vaporization" energy	Reaction energy	Mass of H_2	Mole of H_2O formed	Reaction energy at constant volume, average temperature	Correction to 17° C., constant volume	Q [2 3] 25° C., 1 atm.	Deviation from mean	Series No.
	g	*Int. joules/° C.*	*Joules/° C.*	*Int. joules/° C.*	*° C.*	*° C.*	*Int. joules*	*g*	*Joules*	*Int. joules*	*g*		*Int. joules/mole*	*Joules/mole*	*Int joules/mole*		
1	*1,636.8*	6,844.3	3.6	7,371.3	16.61	*1.773*	13,069.3	0.0164	40.3	13,109.6	*0.09440*	0.046835	279,910	−18	283,250	−2,560	
2	*1,596.0*	6,673.8	3.5	7,200.7	16.49	*1.823*	13,126.9	168	41.3	13,168.2	*.09266*	.045971	286,450	−22	9,790	3,980	
3	*1,641.0*	6,860.2	3.6	7,387.2	17.55	*1.811*	13,378.2	174	42.7	13,420.9	*.09469*	.046979	285,680	24	9,060	3,250	
4	*1,608.9*	6,725.4	3.4	7,272.2	18.01	*1.785*	12,945.2	178	43.7	12,988.9	*.09202*	.045654	284,500	44	7,900	2,090	I
5	*1,591.6*	6,654.2	3.5	7,181.1	17.33	*1.820*	13,069.6	171	42.0	13,111.6	*.09399*	.046631	281,180	15	4,550	−1,260	
6	*1,581.8*	6,614.9	3.6	7,141.8	16.26	*1.853*	132,333.8	161	39.6	13,273.4	*.09489*	.047078	281,950	−33	5,280	−530	
7	*1,604.4*	6,706.4	3.5	7,233.3	18.09	*1.771*	12,810.2	179	43.9	12,854.1	*.09251*	.045897	280,060	48	3,470	−2,340	
8	*1,564.4*	6,542.3	3.5	7,069.2	16.21	*1.833*	12,957.8	160	39.3	12,997.1	*.09294*	.046110	281,870	−35	285,190	−620	
9	*1,586.0*	6,633.0	3.6	7,160.0	16.01	*1.863*	13,339.1	158	38.9	13,378.0	*.09544*	.047351	282,530	−44	5,840	30	
10	*1,641.3*	6,864.4	3.5	7,391.3	15.93	*1.769*	13,075.2	157	38.6	13,113.8	*.09376*	.046517	281,920	−47	5,230	−580	II
11	*1,587.5*	6,637.5	3.5	7,164.4	16.98	*1.841*	13,189.7	168	41.3	13,231.0	*.09432*	.046795	282,750	1	6,110	300	
12	*1,508.9*	6,308.7	3.5	6,835.6	17.10	*1.922*	13,138.0	170	41.8	13,179.8	*.09395*	.046611	282,760	4	6,120	310	
13	*1,558.9*	6,518.4	3.6	7,045.4	16.72	*1.884*	13,273.5	166	40.8	13,314.3	*.09519*	.047227	281,920	−12	5,270	−540	III
14	*1,606.8*	6,717.7	3.4	7,244.5	17.32	*1.786*	12,938.7	171	42.0	12,980.7	*.09227*	.045778	283,560	14	6,930	1,120	
Mean [4]															[5] 285,810	±500	

[1] Heat capacity of calorimeter parts=523.4 international joules/° C.
[2] Correction from constant volume at 17° C. to constant pressure of 1 atmosphere at 17° C.=+3,614 international joules/mole.
[3] Correction from 17° C., 1 atmosphere, to 25° C., 1 atmosphere=−256 joules/mole.
[4] Series I is not included.
[5] This final mean value requires a further correction of −0.017 per cent, or −50 joules per mole, to take care of the fact that the "vaporization" energy correction used in the table includes the work term RT which is not present when water vaporizes at constant volume. Making this correction, we obtain the value 285,760 international joules per mole, with an average deviation of ±500 joules.

Five experiments on the heat of formation of water were reported by von Than [38] who used an ice calorimeter and obtained an average deviation of about ±0.05 per cent in five combustion experiments. Unfortunately, the calibration data of von Than are so few and so lacking in accuracy as to make the high precision of the combustion experiments practically valueless. .

Berthelot [39] reported the result of one experiment. Berthelot and Matignon [40] gave the results of four experiments having an average deviation of ±2,500 joules per mole.

The six results given by Rumelin [41] have an average deviation of ±1,300 joules per mole. The average value of Berthelot and Matignon is about one-half of 1 per cent higher than the usually accepted value while that of Rumelin is lower by nearly the same amount.

The recalculated data of Schuller and Wartha, Thomsen, and Mixter are summarized in Table 10.

TABLE 10

		Number of experiments	"Error"	Combined "error"	Average value	"Error"
			Per cent	*Per cent*		
Schuller and Wartha	Calibration	5	0.080	0.082	285,890	±235
	Combustion	4	.019			
Thomsen	Calibration	0	(.10)	0.24	285,820	±700
	Combustion	3	.220			
Mixter	Calibration	0	(.10)	0.21	285,760	±600
	Combustion	7	.186			

In his recalculation of the data of Schuller and Wartha, Thomsen, and Mixter, Roth obtained for the heat of formation of 18.016 g of water at 18° C., 1 atm., the following values:

Schuller and Wartha	mean cal	68,310
Thomsen	$g=cal._{15}$	68,390
Mixter	do	68,400

Using the factor 4.1875 to convert mean calories into international joules and $\frac{4.185}{1.0004}$ to convert $g=cal._{15}$ into international joules, and correcting the results to 25° C. and 1 atm., and to 18.0156 g of water, one obtains the following values, which are compared with the data recomputed in this paper.

	International joules per mole (18.0156 g) at 25° C. and 1 atmosphere	
	Roth	This paper
Schuller and Wartha	285,820	285,890
Thomsen	285,880	285,820
Mixter	285,920	285,760

[38] See footnote 1 (*h*) and (*j*), p. 2.
[39] See footnote 1 (*k*), p. 2.
[40] See footnote 1 (*l*), p. 2.
[41] See footnote 1 (*n*), p. 2.

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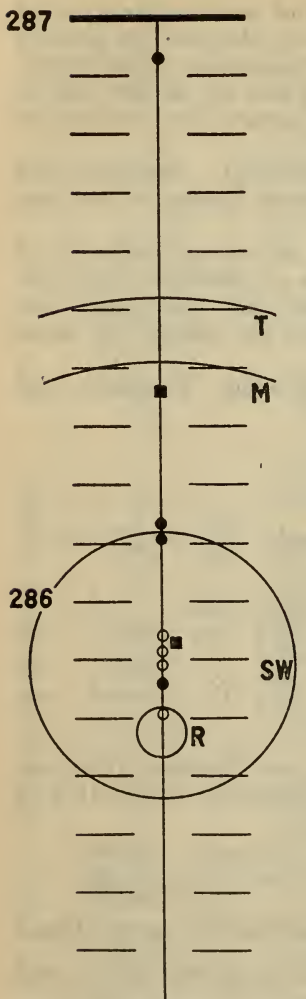


FIGURE 8.—*Plot of the data on the heat of formation of water*

The ordinate scale is in international kilojoules per mole and the data are computed to give the heat of formation of liquid H_2O at 25° C., 1 atmosphere. The points are: ○, Schuller and Wartha; , Thomsen; ; Mixter. The small circle shows the assigned limit of error of the value obtained in the present work, while the other circle and arcs show the assigned errors for the recomputed data.

XIII. CONCLUSION

In the foregoing section, the experimental data of three separate groups of experiments on the heat of formation of water have been recalculated. In Figure 8 are plotted the individual values of these experiments: Four of Schuller and Wartha, three of Thomsen, an seven of Mixter. The "best" value of the present investigation is indicated by the small circle, whose radius is a measure of the assigned error, while the other circles and arcs show the corresponding assigned errors of the other investigations.

Figure 9 shows the individual values of the experiments reported in this paper and the "best" value, together with the average value computed from the data of Schuller and Wartha. The radii of the circles measure the assigned errors in each case. All of the individual values of the present experiments fall within the Schuller and Wartha circle, which in turn is completely inclosed by the Thomsen circle and the Mixter circle, as shown in Figure 8.

A liberal estimate of the sum of all errors in this "best" value deduced from the present experiments is ± 40 joules per mole.

The present data give for the heat of formation of 1 mole (18.0156g) of liquid H_2O, according to the equation,

$$H_{2\,(gas)} + 1/2\ O_{2\,(gas)} = H_2O_{(liquid)} \qquad (20)$$

at 25° C. and a constant pressure of 1 atmosphere, the value[42] 285,775 ± 40 international joules. Using the factor 1.0004 to convert international into absolute joules, and $\frac{1}{4.185}$ to convert absolute joules into g-cal_{15}, this value becomes 285,890 ± 40 absolute joules or 68,313 ± 10 g-cal_{15}. The conversion to absolute joules is subject to revision when a more accurate value is obtained for the relation between the international joule derived from standards maintained at this bureau and the absolute joule.

XIV. ACKNOWLEDGMENT

This work was executed under the direction of E. W. Washburn, and the author is

[42] For small changes in temperature and pressure, the heat of formation of water changes, respectively −32 joules per mole per degree increase in temperature, and −5 joules per mole per millimeter increase in pressure.

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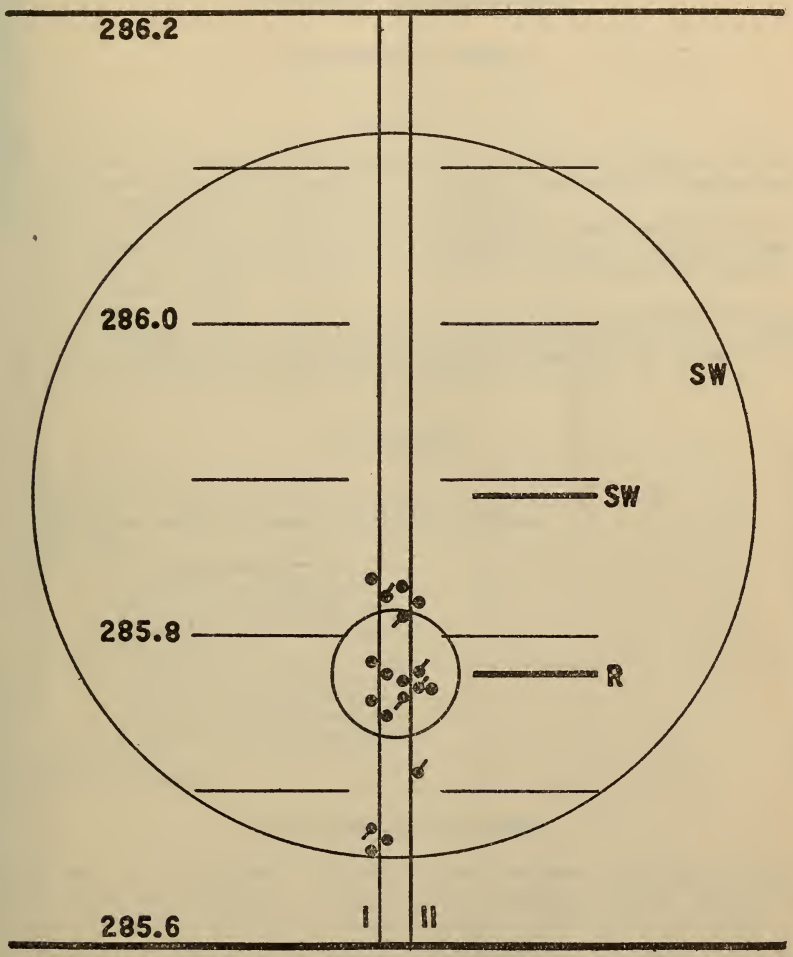


FIGURE 9.—*Plot of the present data on the heat of formation of water*

The ordinate scale gives the heat of formation of liquid H_2O in international kilojoules per mole at 25° C., 1 atmosphere. The O_2 in H_2 experiments are denoted with an appendage. The experiments of Set I are distinguished from those of Set II by the two vertical lines. The average values of Schuller and Wartha and of the present data are shown, together with the "error" circles.

mass, time, thermometry, and standard cell sections of this bureau for their assistance in calibration or analysis. The reaction vessel and gas system were constructed by E. O. Sperling.

WASHINGTON, August 26, 1930.

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