

A RE-DETERMINATION OF THE HEAT OF VAPORIZATION OF WATER

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A number of years ago an improved method for the determination of heats of vaporization of liquids was developed by T. W. Richards and the writer.¹ For testing the method, water was chosen as the substance to be vaporized for three principal reasons: it is a substance easily purified, it has a high heat of vaporization, and it is the substance upon which more methods have been tried than any other; consequently it offered us the best possible means of comparison of our method with the methods used by others.

In the development of the method we finally perfected, after trying a considerable number of devices designed to prevent previously recognized possibilities for error, we discovered some exceedingly important sources of error which had been quite overlooked by other workers. For a detailed description of the apparatus and method, and a complete discussion of the sources of error to be avoided or minimized, the original article must be consulted. Briefly, the method was based on one previously suggested by Kahlenberg,² in which the liquid was vaporized by means of an electrically heated resistance in a specially designed vessel which could be brought close to the condensing coil which was immersed in the calorimeter. In our modification of this apparatus, the water to be vaporized was contained in a vacuum-jacketed cylindrical vessel constructed as shown in Fig. 1. This vaporizing vessel was connected directly to a block-tin condenser immersed in the water of the calorimeter proper, the various parts of which are shown in Fig. 2.

In the calculation of the heat of vaporization of the liquid condensed in the coil, the assumption has always been made

¹ Jour. Am. Chem. Soc., 33, 863 (1911); Proc. Am. Acad. Sci., 46, 511 (1911).

² Jour. Phys. Chem., 5, 215 (1895).

that all of the vapor was at the boiling point of the liquid at the moment that it condensed in the coil. With the various designs of apparatus heretofore used, with the possible exception of that of Luguinin,¹ this assumption is erroneous, for long before the boiling point of the liquid is reached the liquid is giving off vapor which passes into the calorimeter and condenses, and since the heat of vaporization is highly dependent on the temperature of the condensing vapor, the error so introduced into the calculation must have been considerable. Furthermore, in the calculation it has been assumed heretofore that all of the condensed liquid cools from a definite temperature, *viz.*, the boiling point, to the temperature of the calorimeter. This assumption also is not true for the methods previously used, with the exception of that of Luguinin. In our method both of these serious errors are avoided, for the vapor does not begin to pass down the delivery tube to the condensing coil until the liquid has been boiling for some time—the time during which temperature readings are taken to ascertain exactly the correction to be applied for radiation and conduction of heat from the vaporizer to the calorimeter water.

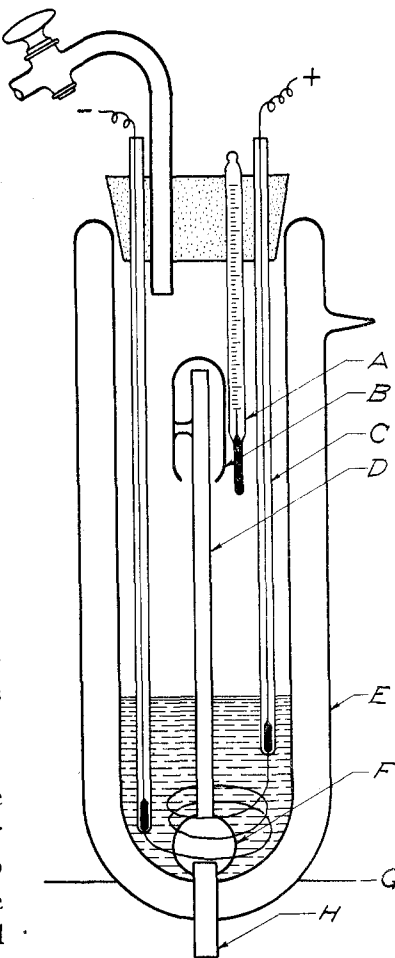


Fig. 1

¹ Ann. Chim. Phys., (7) 7, 251 (1896).

Early in our work it was observed that the values obtained for heats of vaporization depended on the rate at which

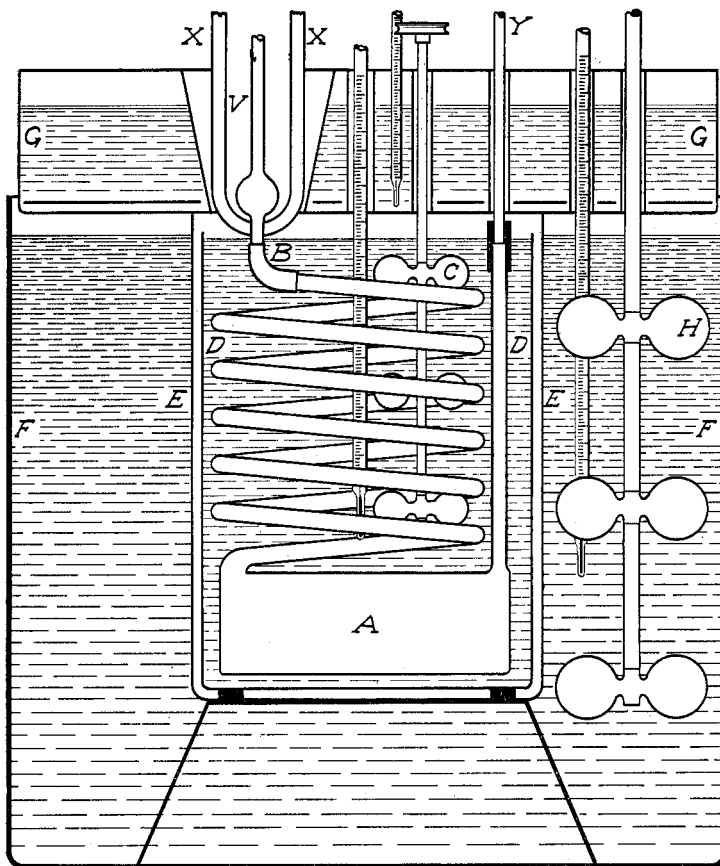


Fig. 2

The calorimeter. The vaporizer (V) is set within a large hole (XX) in the cover. At B is attached the condenser A immersed in water contained in the calorimeter. Between the jacketing vessels E and F is dilute alkali, into which sulphuric acid is dropped in order that the temperature of the surroundings should keep pace with that of the calorimeter proper. C is a stirrer within the calorimeter, H one in the outside vessel

vapor passed into the condensing coil. We succeeded in showing that this effect is due to premature condensation of

the vapor, *i. e.*, condensation of the vapor at some point where the heat given out in the act of condensation would not be transmitted to the calorimeter while the water produced by this condensation would be delivered to the coil. By the introduction of a trap at the bottom of the chamber in which the liquid is vaporized (see F, Fig. 1) and by making the distance from this trap to the calorimeter water as short as possible (a few mm only) the effect produced by this premature condensation was reduced to a minimum. The trap also served to catch and retain any liquid which may have gotten into the delivery tube by spattering. A drop or two of liquid was always found in this trap after the experiment; hence the trap was always emptied between determinations.

While the trap and the shortening of the distance between vaporizer and calorimeter water naturally minimized the effect due to premature condensation, the effect was not wholly eliminated, since it is impossible wholly to eliminate the zone in which premature condensation may take place. To get the true heat of vaporization, however, it is only necessary to conduct several experiments in which the rate of condensation of vapor is made to vary considerably, then plot the times necessary for the condensation of one gram against the values obtained for the heats of vaporization, and by a slight extrapolation of the linear curve so obtained the true heat of vaporization is found, that is, the heat of vaporization which would have been obtained had the vapor passed into the calorimeter under conditions such that no premature condensation could occur.

Curiously, no previous workers have ever made mention of the dependence of the experimental values on the rate of condensation. With the most perfect apparatus we were able to devise, this effect was so marked that serious error would have been made had it not been recognized and corrected for, and with the less perfect methods used by former workers, where the possibility of error was not even recognized, the error must have been very serious indeed since generally the design of apparatus was such as to necessitate considerable premature condensation.

Preliminary work on the heats of vaporization of a number of substances other than water showed the same effect, in degree depending on the difference in temperature between the temperature of the calorimeter and the boiling point of the liquid. Where this difference was great the loss of heat by premature condensation was naturally great; and where the difference was small the effect was small.

Previous to our work it had been noted that the values for the heats of vaporization of liquids as determined by the condensation method were usually lower than the values obtained by the electrical method, where the energy required to vaporize a gram of the material is measured. In this connection it is interesting to find that the values found by our method agree remarkably well with the values obtained by the most refined of the electrical methods, not only for water but for other substances as well. As the average of two closely agreeing series of determinations of the heat of vaporization of a true gram of water at 100° , made with two different vaporizers, the value $538.9 \text{ cal}_{21^{\circ}}$ was found. This value agrees well with the value obtained by Henning,¹ who found the value $539.5 \text{ cal}_{21^{\circ}}$, using a refined electrical method. Work now well under way on the heats of vaporization of a large number of compounds confirms the belief that the values which have been obtained by the electrical methods are not considerably too high, as had formerly been supposed, but rather that the values which have been obtained by the condensation methods are the ones which are at fault.

Soon after the appearance of our paper in 1911, A. W. Smith² published an account of his determinations of the heat of vaporization of water. Proceeding on the assumption that all former condensation methods had necessarily given low results due to "priming," *i. e.*, the carrying over of unvaporized liquid along with the steam, Smith developed a method in which the vaporization took place from a relatively quiet surface. The vaporization was brought about by pass-

¹ Drude's Ann., 21, 849 (1906).

² Phys. Rev., 33, 173 (1911).

ing dry, pre-heated air through the vaporization chamber, the water vapor being subsequently removed from the air by condensing most of it and absorbing the remainder in sulfuric acid. The energy necessary to just overcome the cooling effect of this evaporation, *i. e.*, to maintain the liquid at a constant temperature (98.7°), was supplied electrically, and could be determined by a potentiometric method. By changing the rate of evaporation it was possible to eliminate the necessity of a knowledge of the water equivalent of the apparatus and the amount of heat conducted out through the heating wires, as well as a knowledge of the amount of heat received by the water in the vaporization chamber from the surrounding steam jacket. Since but one temperature was read a complete standardization of the thermometer was unnecessary.

Twenty determinations were made at 98.07° , and the results calculated to 100° . The average of all of these determinations, in which the extreme variation was 2.44 calories, was 540.7 mean calories, or the same number of 15° calories since these are of equal magnitude. The difference between this value and the value which has generally been accepted heretofore was ascribed wholly to priming.

Some fifteen years previous to the work of Smith, Harker¹ had developed a method designed to eliminate danger of error through priming. In this method the vapor was conducted through a pre-heater to insure the removal of all liquid particles before it entered the condensing coil in the calorimeter, the amount of pre-heating being determined by means of a thermo-couple so placed that it gave the temperature of the vapor entering the condensing coil. Correction was made for the excess heat introduced by this pre-heating. Harker concluded from his experiments that the true heat of vaporization of water at 100° is 540 calories. However he considered his experiments to be only preliminary ones, and gave no data. His method has certain features which appear to be somewhat faulty, and likely to give somewhat too high results. These

¹ Mem. Manchester Lit. and Phil. Soc., 10, 38 (1896).

were discussed by Richards and the writer in 1911.¹ The particular virtue of Harker's method lies in the way in which premature condensation was avoided, rather than in the elimination of priming. It is regrettable that further experimentation was not carried out.

Since the question of the possibility of error through priming is so important in measurements of heats of vaporization, it was imperative that the question be subjected to experimental test. Accordingly, the following methods of attack were used:

In the first the heat of vaporization apparatus as used by us at Harvard was set up as for a determination. In the vaporizer was placed a 1 percent solution of potassium permanganate instead of pure water. Now if priming, *i. e.*, the purely mechanical disengagement of liquid particles from the boiling solution, took place, and if these particles were not subsequently removed before condensation took place in the coil it is evident that permanganate should be found in the condensed liquid. Two tests were made, with different rates of vaporization, both of which exceeded the rate used in the measurements of heats of vaporization. In the first 9.3 grams were condensed in three minutes; in the second 15 grams were condensed in three minutes, and in neither case was the slightest trace of permanganate detectable in the distillate. A capillary tube was inserted in the delivery tube of the vaporizer, from beneath, and the trap was washed out with a jet of water. No permanganate was found in the trap. Since these vaporizations were made at a much greater rate (one of them 100 percent greater) than any of the vaporizations in the actual measurements of heats of vaporization, it seems certain that no particles of unvaporized water were carried over mechanically from the boiling liquid in the vaporizer.

The second method of attack was quite different, but perhaps equally as conclusive. In this the vapor above water boiling vigorously in a distilling flask was examined for the

¹ Loc. cit.

presence or absence of particles by observing whether it would show the Tyndall effect. The flask used was one having a wide neck, about 3 cm in diameter. Through this a powerful, condensed beam of light was projected from an arc; the room itself was dark. When the beam of light was brought down to within 5 cm of the boiling water a number of points of light could be seen in the path of the beam, but when it was raised to 10 cm no points of light were observed, even with very vigorous boiling. The water was boiled both by means of the electric current passing through a submerged resistance coil, and by means of a burner placed beneath the flask. In neither case was any semblance of a cone visible.

It therefore seems safe to conclude that in the vaporization which takes place under the conditions of experiment in the measurements made by the method of Richards and the writer no anxiety need be felt regarding the possibility of error through priming. The vapor rising from the boiling liquid has to pass through a hood placed over the upper end of the delivery tube, thence down through this narrow tube to a trap at the bottom of the vaporizer. It is well known to bacteriologists that an effective means of freeing air of bacteria is to pass it through a narrow tube, the inside walls of which are wet. It is also equally well known to those who have occasion to use the ultra-microscope that the most convenient and effective way to get air which is optically empty, *i. e.*, to free it entirely of all suspended matter, is to pass air through such a tube. The chance that particles of liquid torn from the boiling water might traverse all of the pitfalls provided for them in this apparatus and eventually pass into the condensing coil seems very slight indeed; and the first line of experimentation (with the permanganate solution) shows conclusively that unvaporized particles are not so carried over. Doubtless priming does occur under certain circumstances, such as violent boiling under pressure as in steam boilers, but that there is possibility of any uncertainty in the values of heats of vaporization as determined by this particular method seems quite out of the question.

Since the Harvard work was completed the writer has had occasion to build up an entirely new set of apparatus for the measurement of heats of vaporization. In principle the apparatus as it now stands perfected is the same as that used in the former research, the difference being in details of construction.

The two-compartment adiabatic calorimeter formerly used has been replaced by one of the "submarine type,"¹ in which the calorimeter proper is surrounded by one and the same bath of alkali. The stirrer in the alkali bath, of the propellor type, has ten blades and is driven at a high speed by an electric motor. The temperature control in the new form of adiabatic calorimeter is much more satisfactory than in the one formerly used. It is possible to keep the temperature of the outer bath within a few hundredths of a degree of the temperature of the calorimeter proper during the whole determination. The stirring of the liquid in the calorimeter proper is accomplished by means of a stirrer consisting of three flat, perforated brass rings attached to two slender brass rods which pass through tubes soldered into the cover and are fastened to a cross bar of hard rubber which in turn is attached to a stout brass rod which is actuated by an electric motor operating through an eccentric. Both rings and rods are thinly plated with nickel. This stirrer is made to thrust up and down at a lively rate—about 100 strokes per minute—and stirs the water very effectively. The calorimeter proper (of about 1400 cc capacity) is of thin sheet copper, lightly nickel plated inside and out and highly polished to reduce radiation. The condensing coil is of platinum, and has a capacity of about 80 cc. This coil hangs suspended within the stirrer.

To determine the rise in temperature a Beckmann thermometer having a large, long mercury bulb is used. This particular thermometer was selected from a group of a dozen. The scale divisions were fine and sharp, enabling accurate readings to be made. It was standardized by careful com-

¹ See Richards and Jesse: *Jour. Am. Chem. Soc.*, **32**, 268 (1910).

parison with: (1) a Beckmann thermometer which had been standardized by the Physikalisch-Technische Reichsanstalt, corrections for which were given to 0.001° ; (2) an enclosed scale "Normal" thermometer made by Goetze, graduated to 0.01° between 18 and 25° , corrections for which (in thousandths of a degree) had been furnished by the United States Bureau of Standards; (3) a second "Normal" thermometer of similar type, graduated to 0.01° between 14 and 24° , corrections for which (in thousandths of a degree) had been furnished by the Bureau of Standards; and (4) a Leeds and Northrup resistance thermometer and bridge which also had been standardized by the Bureau of Standards. Temperatures could be estimated to 0.0005° by means of this thermometer and bridge.

Comparisons of all of these thermometers were made at the same time, under *adiabatic conditions*. One observer read the mercury thermometers while a second manipulated the bridge. All the thermometers were read at least twice for each point at which comparisons were made, these points being at intervals of about 0.1° throughout the Beckmann scale. The comparisons showed the mercury thermometers and resistance thermometer standardized by the Bureau of Standards to be consistent among themselves, within the limit of error of reading, while the readings taken from the thermometer standardized by the Reichsanstalt did not agree so well with the thermometers standardized by the Bureau. For this reason more reliance was placed on the thermometers standardized by the Bureau in calculating the corrections to be applied to the thermometer used in this research. The thermometers were compared in a room whose temperature was regulated to 20° – 21° , since the thermometer being standardized was to be used in a room maintained at this temperature.

The greatest single improvement in the apparatus over that previously used consists in the substitution of a vaporizer made of thin, transparent quartz for the vaporizers made of glass. Considerable difficulty was experienced in even getting the glass vaporizers made, to say nothing of the danger

of breakage under the severe strains they were subjected to in service. Although the initial cost of such a complicated piece of quartz apparatus is considerable it is in the long run more economical than glass on account of the decreased breakage.¹ The position of the quartz vaporizer was carefully adjusted so that the level of the water in the calorimeter came up about one centimeter higher than the point where the delivery tube joins the outer wall of the jacket. This depth of immersion is necessary because a great deal of heat is undoubtedly liberated in the portion of the quartz tube which dips into the water of the calorimeter. The vaporizer was always maintained in exactly this same position, so that the water equivalent of the system should remain constant. If in different determinations different amounts of surface of the quartz were wetted the water equivalent naturally would vary.

Water Equivalent

The accurate determination of the water equivalent of the calorimetric system heated by the condensing vapor presented some difficulties. The equivalent of the calorimeter proper, stirrer, condensing coil and thermometer can be calculated with sufficient accuracy (assuming that the specific heats are sufficiently well known), but the determination of the equivalent of the part of the quartz vaporizer immersed in the water cannot be calculated directly. The problem was solved in the following manner: First, the total water equivalent of the entire calorimetric system was determined by an electrical method, then the quartz vaporizer was removed and the total water equivalent again determined. The difference between these two values must represent the water equivalent of the quartz, and this value can be added to the value calculated for the rest of the calorimetric parts. It is of course necessary that the quartz be immersed *always to the same depth*, else the water equivalent of the sys-

¹ The quartz apparatus used in this work was made by The Hanovia Chemical and Manufacturing Co., of Newark, N. J.

tem will vary. This condition was met by fixing the vaporizer in the cover of the calorimeter so that it was always in the same position; then to secure the same depth of immersion it is only necessary that the same volume of water be placed in the calorimeter each time.

The apparatus was set up exactly as used in the measurement of heats of vaporization, with the following exception: On account of lack of room in the calorimeter for both, the platinum condensing coil was removed and in its place was substituted an electrical heating element consisting of a suitable length of fine nichrome wire to give a resistance of about 32 ohms, contained in a thin, flat metallic sheath. The wire was wound on a mica frame and was enclosed in a flat brass case 5 cm long, 4 cm wide and 3 mm thick, to which was soldered a light brass tube 13.5 cm long and 4 mm in diameter. One end of the nichrome wire was soldered to the bottom part of the case, the other being soldered to a stout rubber-insulated copper wire which passed out the tube. The wire on the mica frame was insulated from the containing case by thin mica sheets, one on each side of the frame. The resistance element so prepared was given a light coating of copper, on which was then deposited a thin layer of silver. In calculating the water equivalent of this element the assumption was made that it was composed entirely of brass, since the weights of nichrome, mica, copper and silver are, when taken together, not more than two grams.

The heating element was placed in such a position that the sheath containing the resistance wire was about at the center of the calorimeter. The tube of the element passed through dry corks fitting tightly into a brass tube soldered into the cover of the calorimeter. The current was brought to the heating element by heavy (No. 10) insulated copper wire. Connection was made through freshly brightened brass connectors, with set screws, to secure perfect electrical contact. Two No. 10 insulated copper wires were soldered to the leads carrying the current, the junction of the wires being about one centimeter back of the connectors. These wires led to a

heavy double-pole, double-throw switch, by means of which either a voltmeter or potentiometer could be bridged across the circuit at will, to ascertain the potential drop across the terminals of the heating element.

With the heating element so placed, the amount of water necessary to bring the level to the desired point on the quartz vaporizer was carefully determined, and this exact amount of water was used in all of the determinations.

The calculation of the water equivalent of the apparatus by the electrical method can best be described by means of a sample calculation. The symbols used have the following significance:

- H = the water equivalent of the calorimetric parts,
- Q = the quantity of heat (in 20° calories) liberated by the passage of the current through the element,
- W = the weight (reduced to *vacuo*) of the water in the calorimeter,
- R = the rise in temperature of the calorimetric system,
- E = the potential drop across the terminals of the heating element,
- F = the value of the faraday in coulombs (96490),¹
- w' = the weight of silver deposited in the coulometer.

The data for the following calculation were obtained with the quartz vaporizer in place:

Data:

Weight of water in calorimeter (W)	1376.5 grams
Rise in temperature of the system (R)	4.820°
Voltage drop across terminals of heating element (E)	35.000 volts
Weight of silver deposited in coulometer (w')	0.9162 gram
Mean temperature of calorimeter	19.4°
Value of the calorie at this temperature	4.180 joules

Calculation:

$$H = \frac{Q - (W \times R)}{R}$$

But,

$$Q = \frac{(F \times w' \times E)}{(107.88 \times 4.180)} = \frac{(96490 \times 0.9162 \times 35.000)}{(107.88 \times 4.180)}$$

¹ Value found by the Bureau of Standards, using the silver coulometer.

Then,

$$H = \frac{\left(\frac{96490 \times 0.9162 \times 35.000}{107.88 \times 4.180} \right) - (1376.5 \times 4.820)}{4.820}$$

$$H = 47.0 \text{ grams.}$$

It will be observed that the quantities which have to be determined are: (a) the weight of water in the calorimeter, (b) the rise in temperature of the system, (c) the voltage drop across the terminals of the heating element, and (d) the weight of silver deposited in the calorimeter.

The water used was freshly distilled from alkaline permanganate. A definite quantity was placed in the calorimeter, the weight being constant to 0.05 gram. The weighing was done on a large Bunge balance capable of carrying a load of 2 kilos with a sensitiveness of one-tenth milligram. This filling of the calorimeter was left for the last operation before putting on the cover, in order to minimize evaporation. The amount of water evaporating from the calorimeter during a determination was negligible, as the volume of air in the compartment occupied by the calorimetric system was very small; and the brass tubes through which were inserted the thermometer, heating element and quartz vaporizer were entirely closed, to prevent circulation of air through them. For the same reason the brass rods of the stirrer passed through closely fitting cork sleeves. The weights of water used in the calorimeter were therefore certain to one or two parts in fourteen thousand.

The temperature rise was determined with the carefully standardized thermometer, already described. The temperature of the room was automatically controlled by a thermostatic device, and was kept at the temperature at which the thermometer had been standardized; hence no correction for exposed mercury thread was necessary. The temperature of the system was read at intervals of one minute for some time before the current was turned on to the heating element, and was read similarly for some time after the current had been turned off. A small electric buzzer attached

to the top of the thermometer eliminated the sticking of the mercury thread. The temperature readings were made with the aid of a reading telescope mounted on the thermometer. The scale was illuminated from behind; the readings to 0.001° could be made with certainty. The maximum temperature (which of course remained constant, as conditions were adiabatic) was attained within one minute after the current ceased passing through the heating element. The temperature rise, usually about 4.8° , took place at the rate of about 0.4° per minute, and of course took place regularly. As the zero of the Beckmann thermometer in the bath of alkali had been set identical with the zero of the Beckmann in the calorimeter (to 0.01°), it was easy to admit sulphuric acid into the violently agitated alkali at such a rate that the temperatures of the calorimeter and its environment did not differ by more than 0.05° at any time and were usually within 0.01 or 0.02° . One observer (my assistant, Mr. R. V. Williamson, to whom I am greatly indebted) devoted his entire attention to the adiabatic control of the calorimeter throughout the whole experiment. The readings of temperature rise are probably as certain as temperatures can be read with the mercury thermometer, *i. e.*, to within $\pm 0.001^{\circ}$. The temperature rise was therefore certain to about one or possibly two parts in five thousand.

The current for the heating element was taken from a group of storage batteries, isolated from the remaining batteries in the battery room. The potential drop required to give the desired rate of temperature rise was 35 volts. In a number of preliminary experiments made to test the method and to become familiar with the exacting technique required, a large Weston Laboratory Standard voltmeter with 12-inch scale was used to ascertain the voltage. This voltmeter was standardized by means of a Brooks potentiometer and a standard Weston cell, certification of which had been made by the Bureau of Standards.¹ By means of a five-inch lens

¹ This standardization was made by Mr. F. A. Kartak, Director of the Wisconsin Standards Laboratory, to whom I am greatly indebted.

mounted above the scale, readings to 0.02 volt could be estimated. By means of a suitable sliding resistance, the potential drop could be kept constantly at 35 volts to within ± 0.02 volt. As a part of the current passed through the voltmeter a correction had to be made for the amount of energy so lost. This was determined by putting the voltmeter in series with a silver coulometer, with the voltmeter registering 35 volts, and determining the amount of silver deposited at the end of several hours. The correction so found amounted to about 0.14 percent of the total current used, and agreed closely with the correction as calculated from the known resistance of the voltmeter (about 31,000 ohms) and that of the heating element (about 32 ohms).

It was feared, however, that the voltmeter readings might not be sufficiently accurate and certain, and in the final work here reported a Leeds and Northrup Type K potentiometer and Weston standard cell were substituted for it. A volt box with a ratio of 1 to 100 was used to reduce the potential drop to a value which could be measured accurately. The volt box was improvised from a large Wolff resistance box, having a total resistance of approximately 100,000 ohms, the individual resistances of which as well as the total were standardized by means of a large Leeds and Northrup Wheatstone bridge having 10 ratio coils. In this standardization a Leeds and Northrup Type HN wall galvanometer was used as indicating instrument. The total resistance of the box was found to be 99,937 ohms, while the sum of the individual resistances, as measured separately, was 99,934 ohms. The resistance value for the particular 1000 ohm cell used to pick off potential drop for the potentiometer was checked and re-checked using different combinations of the ratio coils, all of which gave closely agreeing values. The mean of these values showed this coil to have a resistance of 999.83 ohms. The volt box therefore had a ratio of $\frac{999.83}{99934}$. To secure a potential drop of exactly 35 volts required that the potentiometer be set to read $\frac{999.83}{99934} \times 35 = 0.35017$ volt.

The indicating instrument used with the potentiometer was a Siemens and Halske galvanometer having a very short period and giving a deflection of 1 mm on a scale 1 meter distant for a potential of 12×10^{-7} volts. The sensitiveness was somewhat further increased by increasing the distance to 120 cm.

The sliding contact rheostat already mentioned was supplemented by placing in series with it a coarse slide wire of manganin, whose traveling contact was operated by a micrometer adjustment. The sensitiveness of the galvanometer was such that a movement of 2 mm for the slider produced a noticeable deflection on the scale. It was found possible to maintain the voltage constant to ± 0.001 volt.

The Weston standard cell used with the potentiometer was one which was kindly loaned by the Wisconsin Standards Laboratory. It had been standardized a few months previously by the Bureau of Standards, and was compared at the time of use with a similar Weston cell which had been standardized by the Bureau more recently. This comparison was made by means of an excellent Wolff potentiometer in the Wisconsin Standards Laboratory. The value agreed well with that previously found by the Bureau. The potential of this cell was 1.01872 at 21.5° .

The coulometer used was of the Richards porous cup type, platinum dishes of about 275 cc capacity being used as cathodes, and electrolytic silver as the anode. The unglazed porcelain cup was cleaned by digestion with hot nitric acid for several hours, after which the acid was completely removed by repeatedly washing and soaking in pure water until the water showed no acid reaction. While not in use the cup was kept immersed in silver nitrate solution. The electrolyte was made from Merck's pure silver nitrate, which was found to be neutral. A 10 percent solution was used, fresh portions being used for each determination. The precautions recommended by the Bureau of Standards¹ were observed in handling and drying the silver deposit. The de-

¹ Bull. Bureau of Standards, 13, 479 (1916).

posits were weighed on a Spoerhase-Staudinger balance, sensitive to $\frac{1}{50}$ th milligram, the weighings being made with a set of platinum plated Sartorius weights which had been standardized by the Bureau of Standards. As the deposits weighed about 0.9 gram, it is felt that the amounts of current used were determined to one part in nine thousand.

Having assembled the various parts of the apparatus, the approximate resistance to maintain a potential drop of 35 volts across the terminals of the heating element was determined by putting in a coulometer similar to the one to be used in the determination and adjusting the rheostat to the position required to give a reading of 35 volts on the voltmeter. This coulometer was then removed and the one to be used was put in its place; and the potentiometer was bridged in, in place of the voltmeter, by means of the double throw switch. Meantime the adiabatic bath was being adjusted to the proper temperature and readings of the temperature of the calorimetric system were made at intervals of one minute. When all was in readiness, the initial temperature thus having been determined exactly, the current was turned on and the necessary slight adjustment was quickly made on the rheostat (or extended wire) to bring the voltage precisely to 35 volts. One observer watched the galvanometer and kept the voltage constant by keeping the galvanometer indication at zero by means of the slide wire, while the other gave his entire attention to the exact control of the adiabatic bath. When the desired rise in temperature, about 4.8° , had been attained, the current was cut off and temperature readings were again taken for some time at intervals of one minute. The initial and final temperatures were read on stationary mercury threads, the temperature of the calorimeter remaining constant during the two periods. The coulometer was dismantled immediately the current was cut off and the deposit of silver was washed and dried, the washings being examined for particles of disengaged silver. In none of the runs here reported were weighable amounts of silver found in the wash-water.

The data and results for the six determinations made to ascertain the water equivalent of the calorimeter and parts, with the quartz vaporizer in place, appear in the following table:

TABLE I

Weight of water in calorimeter (<i>vacuo</i>) Gms	Rise in temperature °	Mean temperature of calorimeter °	Voltage drop across heating element	Weight of silver deposited Gm	Total water equivalent Gms	Water equivalent of all calorimetric parts Gms
1376.5	4.810	20.3	35.000	0.9137	1422.6	46.1
1376.5	4.769	20.3	35.000	0.9065	1423.5	47.0
1376.5	4.820	20.2	35.000	0.9162	1423.5	47.0
1376.5	4.812	20.2	35.000	0.9147	1423.6	47.1
1376.5	4.793	20.2	35.000	0.9103	1422.5	46.0
1376.5	4.868	20.2	35.000	0.9254	1423.7	47.2

Mean value = 1423.2 gms 46.7 gms

Since the heating element was substituted for the platinum condensing coil (there not being room for both) a calculation had to be made to determine what change in water equivalent was caused by this substitution. The weight of the heating element was 52.5 grams. Considering this as being composed entirely of brass, its water equivalent was $52.5 \times 0.091 = 4.78$ grams. Since the water equivalent of the condensing coil was $150.3 \times 0.032 = 4.81$ grams, the difference in water equivalent caused by the substitution of the heating element for the platinum coil is negligible. Hence the water equivalent of the calorimetric parts of the apparatus as assembled for measurements of heats of vaporization would appear to be 46.7 grams.

The quartz vaporizer was then removed and four determinations of the water equivalent of the system remaining were made in precisely the same manner. The data and results calculated therefrom appear in the following table.

From the results shown in these two tables it is evident that the amount to be added for the water equivalent of the quartz is $1423.2 - 1419.0 = 4.2$ grams.

TABLE II

Weight of water in calorimeter (<i>vacuo</i>) Gms	Rise in temperature °	Mean temperature of calorimetric °	Voltage drop across heating element	Weight of silver deposited Gm	Total water equivalent Gms	Water equivalent of all calorimetric parts Gms
1376.5	4.836	20.3	35.000	0.9162	1418.8	42.3
1376.5	4.293	19.9	35.000	0.8134	1419.0	42.5
1376.5	4.839	20.2	35.000	0.9166	1418.6	42.1
1376.5	4.830	20.2	35.000	0.9155	1419.5	43.0

Mean value = 1419.0 gms 42.5 gms

The water equivalent of the entire apparatus composing the calorimetric system may now be calculated.

The copper calorimeter was made with tightly crimped joints to minimize the amount of solder required to make it tight. The amount of nickel used in plating was small, and since its specific heat is nearly that of copper the entire calorimeter can be considered as being composed of copper. As its weight was 275.2 grams and the specific heat of copper at 20° is 0.093, the water equivalent of the calorimeter was 25.59 grams. The stirrer was made of brass and was lightly plated with nickel. Since but a small length of the brass rods projected above the calorimeter, where they were fastened to the hard-rubber cross piece, the entire weight of the stirrer was taken in calculating its water equivalent. Its weight was 90.9 grams. Taking the specific heat of brass to be 0.091 at 20° the water equivalent for the stirrer would be 8.27 grams. The condensing coil was made of platinum and, as mentioned above, its water equivalent was $150.3 \times 0.032 = 4.81$ grams. The water equivalent of that portion of the Beckmann thermometer which was immersed in the calorimeter water (the depth of immersion of course always being the same) was determined by the method of Ostwald,¹ and was found to be 1.74 grams. The sum of all of these quantities, including the value found for the quartz, was 44.6 grams.

¹ Ostwald-Luther: "Physico-chemische Messungen," p. 300 (1910).

It will be noted that the value obtained by the electrical method for the water equivalent of the various parts is about two grams higher than the value obtained by calculation from the known weights and specific heats of the parts. It must be remembered, however, that this difference is really a difference of two grams in fourteen hundred and twenty rather than two grams in forty-four, since by the electrical method the water equivalent of the parts is gotten by difference, *i. e.*, the total water equivalent minus the water equivalent of the water placed in the calorimeter. Because of a difficulty which is inherent in the electrical method, and for which no really satisfactory correction can be made, *viz.*, the error which may arise from the possible flow of heat out of the calorimeter along the stout copper wires used to carry the electric current for heating, perhaps more reliance should be placed on the value for the water equivalent as determined by calculation from the known weights and specific heats, although the electrical measurements were made with the utmost care. The temperature of the room, during the measurements made by the electrical method, was maintained at a point 0.5 to 1.0° higher than the mean temperature of the calorimeter, to minimize the tendency for heat to flow out of the calorimeter during the heating period. The fact that the initial readings and final readings of the temperature of the calorimeter, surrounded by its adiabatic bath, remained constant showed that no appreciable quantity of heat was flowing out from or into the calorimeter along the copper wires during either of these periods. Moreover the resistance wire in the heating element was inclosed in a very thin, flat sheath which was immersed several centimeters under the level of the well-stirred calorimeter water. The heat must have been given up very quickly to the calorimeter water because of the construction of the element, a conclusion which is further supported by the fact that after the current was shut off the temperature ceased to rise almost immediately. It seems unlikely that either the tube supporting the sheath or the copper wire running through this tube were at a temperature

appreciably higher than the calorimeter water, hence there should have been little, if any, loss of heat by conduction out of the system along the copper wires attached to the heating element. However this possible source of error may be responsible for the small difference in the total water equivalent (a difference of but 0.14%) as determined in the two ways. Of course there remains one other alternative; the specific heats of the substances composing the calorimetric system may not be known with sufficient accuracy. Should it later develop that such is the case a recalculation can be made from the data here reported. In the calculations of the heat of vaporization of water reported in this paper I have used the value calculated from the weights of the various parts and the specific heats which seem to be most reliable. The electrical measurements have been used to ascertain the water equivalent of that part of the quartz vaporizer which is wetted by the calorimeter water when the apparatus is in use.

Since the correctness of the value for the heat of vaporization is dependent on a very exact knowledge of the water equivalent of the apparatus, it seemed desirable to check this value by an additional method. This third method consisted in introducing into the condensing coil of the calorimeter a quantity of hot water, at a known temperature, noting the rise in temperature of the calorimetric system, and ascertaining the quantity of water by weighing the coil after dismantling the apparatus. This method will be referred to in this paper as the "hot water method."

The apparatus used was one designed in collaboration with T. W. Richards in 1908 for the determination of the specific heats of liquids, and has not previously been described. The water is heated, by an electrically heated resistance coil of platinum wire, in a container closely resembling the vaporization flask already described. This vessel (see Fig. 3) is made of transparent quartz, is vacuum jacketed, and the inner walls (*i. e.*, in the vacuum chamber) are silvered to about half the height of the vessel. Passing through the bottom of this flask is a short delivery tube, into the top of which is

ground a long quartz capillary tube, which serves as a tight stopper. The platinum condensing coil is attached to the

lower end of this delivery tube, the end of the platinum spiral being flared somewhat so that the delivery tube sets down into it a few millimeters. Connection between the two is made by a very short piece of rubber tubing. The outside dimensions of this quartz vessel are approximately the same as those for the vaporizer. Care was taken to immerse this new vessel to the same depth that the quartz vaporizer is immersed in measurements of heats of vaporization.

A delivery tube passing out through the stopper and to a condenser allows the escape of steam while the water is being boiled.

A Landsberger thermometer graduated to 0.05° and capable of being read to 0.01° was inserted through the stopper, with its bulb immersed in the water. The entire mercury thread was within the flask, the reading being made through the walls with the aid of a reading lens.

A suitable quantity of pure, freshly distilled water was placed in the flask and was boiled for some time by the cur-

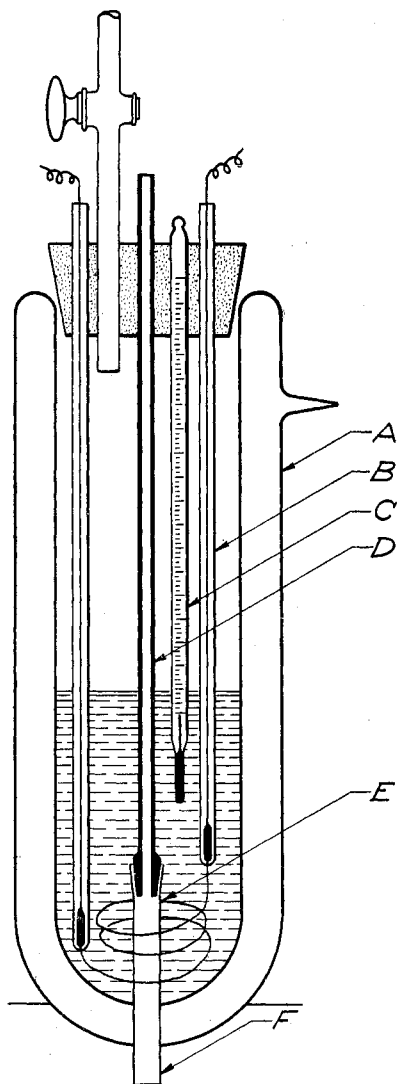


Fig. 3

rent. Readings of the temperature of the calorimetric system were taken for some time, at intervals of one minute. After the temperature rise per minute had thus been ascertained with certainty, and the exact temperature of the boiling water had been noted, the boiling was discontinued by opening the line switch, the quartz stopper was immediately raised for the few seconds necessary for the desired quantity of water to run into the coil in the calorimeter, the stopper was again inserted and boiling resumed by closing the switch. The platinum heating coil in the boiling chamber was always placed below the top of the delivery tube, so that it was always entirely immersed in water. Immediately the water began to run into the platinum condensing coil in the calorimeter, acid was delivered into the alkali bath at a rate such that the temperature of this bath rose simultaneously with that of the calorimeter. Since the boiling was interrupted for but a few seconds, the temperature of the water remaining in the flask did not change appreciably, and consequently the radiation and conduction of heat to the calorimeter remained regular. Although the delivery of the water took but a few seconds (about fifteen) all of its heat was not given up so quickly. In fact about ten minutes were required for the delivery of all of the heat to the calorimetric system. Temperature readings were taken at intervals of one minute until the successive readings differed by the same amount, showing that the water in the coil had ceased to give out heat to the calorimeter. This amount of change per minute is naturally somewhat less than the change per minute in the fore period, since the difference in temperature between the boiling chamber and the calorimeter system has been diminished by about five degrees, and also because of the fact that the water equivalent of the system in the after period is some sixty or so grams greater than it was in the fore period.

The amount of water entering the coil can be determined exactly by weighing. However, the 18 mm of quartz delivery tube immersed in the calorimeter water has its internal walls wetted by the water flowing through it, and usually one small

drop was found hanging inside this tube when the apparatus was dismantled. Since the heat that was contained in this water left in the delivery tube was transmitted to the calorimeter water it is necessary to know approximately how much was left in the tube. It was estimated that this amounted, on the average, to about 0.1 gram. It certainly was not less than this amount, nor was it probably more than 0.15 gram. In the calculations following, a correction of +0.1 gram has been made to the weights of water actually contained in the platinum coil.

It was necessary to know very exactly the temperature at which the water was delivered to the coil. The thermometer used for this purpose could easily be read to 0.01° , but to get this degree of accuracy it was necessary to determine the thermometer correction after each experiment. Immediately after use each time, the correction to be applied to the reading of the boiling point of water was determined by hanging the thermometer in live steam in a thermometer tester, the whole instrument being in the steam. The temperature of the steam was ascertained by reading the barometer, applying the necessary corrections and consulting the tables. The barometer was of the Weather Bureau type and was standardized by comparison with the United States Weather Bureau Barometer at the Madison station.

The method of calculation can again best be shown by an example.

Data:

Time when reading was taken	Observed thermo- metric reading (uncorrected)	Increase in tempera- ture per minute
II : 05	0.307°	
II : 06	0.329	0.022
II : 07	0.351	0.022
II : 08	0.373	0.022
II : 09	0.396	0.023
II : 10	0.419	0.023
II : 11	0.442	0.023
II : 12	0.464	0.022
II : 13	0.486	0.022
II : 14	0.508	0.022
II : 15	0.530	0.022
II : 16	0.552	0.022
II : 17	0.574	0.022
II : 17 Water run into coil		
Current off 16 seconds		
II : 21	4.140	
II : 22	4.198	0.058
II : 23	4.239	0.041
II : 24	4.270	0.031
II : 25	4.296	0.026
II : 26	4.320	0.024
II : 27	4.343*	0.023
II : 28	4.365	0.022
II : 29	4.386	0.021
II : 30	4.408	0.022
II : 31	4.429	0.021
II : 32	4.450	0.021
II : 33	4.471	0.021

	As read from Beckmann	Correction to reduce to true temperature	True temperature hydrogen scale
Final temperature	4.343°	17.772°	22.115°
Initial temperature	0.574	17.754	18.328

Rise in temperature 3.787°

* Point at which water in coil ceased to give out heat.

Rise due to radiation and conduction = $10 \times 0.0215 =$	0.215°
Rise in temperature due solely to heat given out by cooling of water run into coil	3.572°
Mean temperature of calorimeter	20.2°
Barometric pressure (corrected)	743.8 mm
True temperature of steam in thermometer tester	99.40°
Thermometer reading for steam in tester	99.26°
Correction for thermometer	+0.14°
Thermometer reading for boiling water	99.58°
True temperature of boiling water	99.72°
Heat given out by cooling of one gram of water from the boiling temperature to the mean temperature of calorimeter = $(99.72 - 20.22) \times 1.0012 =$	79.60 cal
Weight (reduced to <i>vacuo</i>) of water run into coil	60.64 gms
Water equivalent of water placed in calorimeter	1276.25 gms
Water equivalent of $\frac{1}{2}$ the water run into the coil	30.32 gms
Total water equivalent for water	1306.57 gms
Water equivalent of calorimetric parts = $\left(\frac{60.64 \times 79.60}{3.572} \right) - 1306.6 =$	44.7

Five determinations of the water equivalent of the apparatus were made in this manner. The data and results calculated therefrom appear in the following table:

TABLE III

Weight of water in calorimeter (<i>vacuo</i>) Gms	Weight of water delivered to coil (<i>vacuo</i>) Gms	True rise in temperature of calorimeter °	Temperature of boiling water °	Mean temperature of calorimeter °	Total water equivalent Gms	Water equivalent of calorimetric parts Gms
1276.25	65.53	3.833	99.36	20.22	1354.6	45.6
1276.25	54.71	3.230	99.46	20.01	1347.3	43.7
1276.25	62.01	3.646	99.45	20.07	1351.5	44.3
1276.25	68.11	3.985	99.69	20.40	1356.8	46.5
1276.25	60.64	3.572	99.72	20.22	1351.3	44.7
Mean =						45.0

This value of 45.0 grams represents the water equivalent of the calorimetric parts when the quartz boiling vessel is substituted for the quartz vaporizer. Although the two quartz vessels are nearly alike in size and were immersed to the same depth they do not have the same water equivalent because of the fact that the boiling vessel was made of

considerably thicker quartz. It was therefore necessary to determine the amount that the quartz played in fixing the value for the total water equivalent. This was accomplished by the electrical method already described. The assembly of apparatus for this purpose was precisely the same as described for the determination of the total water equivalent of the apparatus when the quartz vaporizer was included in the set-up, except that the vaporizer was replaced by the boiling-vessel. The difference between the two total water equivalents of course gave the difference between the water equivalents of the two quartz vessels, or rather the parts of each concerned in making up the total water equivalent in each case, and enables us to correct the values for the water equivalent as obtained by the "hot water method." The data for the determinations and the results of the calculations made therefrom appear in the following table:

TABLE IV

Weight of water in calorimeter (<i>vacuo</i>) Gms	Rise in temperature °	Mean temperature of calorimeter °	Voltage drop across heating element	Weight of silver deposited Gm	Total water equivalent Gms	Water equivalent of all calorimetric parts Gms
1376.5	4.670	20.23	35.000	0.8893	1426.1	49.6
1376.5	4.716	20.16	35.000	0.8963	1423.4	46.9
1376.5	2.409	19.03	35.000	0.4586	1425.6	49.1
1376.5	4.222	19.91	35.000	0.8033	1424.9	48.3
1376.5	4.814	20.25	35.000	0.9150	1423.5	47.0
1376.5	4.794	20.27	35.000	0.9124	1425.4	48.9
1376.5	4.810	20.36	35.000	0.9143	1423.5	47.0
1376.5	4.798	20.32	35.000	0.9126	1424.5	48.0
Mean value 1424.6 gms						48.1 gms

Water equivalent of all calorimetric parts when quartz vaporizer is included in set-up 46.7 gms

Water equivalent of all calorimetric parts when quartz boiling vessel is substituted for vaporizer 48.1 gms

Difference due to substitution of boiling-vessel for vaporizer 1.4 gms

From this it is evident that the values obtained for the calorimetric parts as determined by the "hot water method" should be diminished by 1.4 grams to get the value for the parts as used in the measurements of heats of vaporization. This gives 43.6 grams as the water equivalent of all calorimetric parts of the system so set up, whereas by direct calculation from the known weights and specific heats, plus the value which had to be added for the quartz vaporizer (as obtained by the electrical method) the value 44.6 grams was found. Since the total water equivalent for the determinations of heats of vaporization is about 1325 grams, the difference in total water equivalent for these determinations as determined by these two methods is about 1 part in 1325, or a difference of about 0.07 percent.

As the "hot water method" is one which would be likely to give slightly low rather than high results, because of the possibility of loss of heat while the water is running from the boiling chamber into the coil below, more reliance is placed in the other method. In the "hot water method," the water flows through a quartz tube about 53 mm long, the upper 30 mm of which is surrounded at all times during the determination with boiling water, 5 mm of which is between the inside and outside walls of the vacuum jacket, and the remaining 18 mm of which is submerged in the calorimeter water. No loss of heat can occur in the first zone of 30 mm, since this is at all times at the temperature of the boiling water, and probably very little occurs in the second narrow zone of 5 mm, while the heat given out in the third zone is all transmitted to the calorimeter water. The only loss of heat therefore takes place in the very narrow zone between the walls of the flask. This loss, however, must be small, since the zone is narrow, the water passes through it very quickly, it is considerably warmed before the water begins to pass through it (by conduction of heat from the boiling liquid above), thus causing the temperature gradient to be reduced, the tube passing through this zone is well silvered, and the space between the walls is highly evacuated. These reasons for the

small loss of heat in this zone undoubtedly account for the really excellent agreement between the two methods, an agreement which is extremely reassuring as to the accuracy of the value for the water equivalent of the heat of vaporization apparatus.

Heats of Vaporization

Having described the changes in detail made in the apparatus for the measurement of heats of vaporization and having discussed the methods whereby the water equivalent of the apparatus was determined, we may now proceed to the measurements of the heat of vaporization themselves.

In the first half of the new series of determinations the temperature of the steam entering the condensing coil was determined from the existing atmospheric pressure; in the latter half the temperature of the steam as it entered the delivery tube was taken with a standardized thermometer capable of being read to 0.01° . In a number of the determinations in the first half of the series a water-filled manometer was connected with the vaporization chamber. At no time was there ever any change of pressure sufficient to cause an appreciable error in the determination of the temperature of the steam. What little difference there was, never more than a few mm of water pressure, was negative, *i. e.*, the pressure in the vaporization chamber was slightly less than the atmospheric pressure existing at the time. This difference in pressure was usually greatest toward the end of the run, and for the greater portion of the experiment was very slight indeed. The difference in pressure was not sufficient to cause an average error of 0.01° for the experiment.

Since the vaporizations took place at varying atmospheric pressures, none of which were as great as 760 mm the values obtained at the different temperatures of vaporization had to be corrected to 100° in order that they might be plotted. This correction was made by the formula deduced by Henning¹ for the change in heat of vaporization of water with temperature, the formula being

$$L = 94210 (365 - t^{\circ})^{0.31249} \text{ cal.}$$

¹ Loc. cit.

In the neighborhood of 100° , the change of heat of vaporization, as determined by this formula, is $0.63 \text{ cal}_{15^{\circ}}$ per degree. The values obtained have all been corrected to 100° by this equation, as is shown in the table. The correction usually amounted to about two-thirds of a calorie. The following table shows the data and results obtained for twenty-one determinations of the heat of vaporization of water made at quite different rates of vaporization, all determinations in which the technique was known to be faulty having been excluded from the table.

The accompanying graph (Fig. 4) shows the dependence of the values obtained on the rate of condensation. As was pointed out in the former paper, and discussed at considerable length, there is every reason to believe that the curve should be a linear one; and this conclusion has been verified repeatedly, not only for the heat of vaporization of water but for the heat of vaporization of a large number of other liquids as well, data and results for which will be published in the near future. A straight line drawn through the points plotted shows that the heat of vaporization of a true gram of water at 100° is $539.9 \text{ cal}_{20.5^{\circ}}$.¹ In terms of the 21° calorie this becomes $539.8 \text{ cal}_{.}$, and as the 21° calorie is about 0.9985 times the 15° calorie, in terms of the latter the value is 539.0 .

The new value for the heat of vaporization of water is in good agreement with the values obtained with the Harvard apparatus and published in 1911, the value reported at that time being $538.1 \text{ cal}_{15^{\circ}}$. The difference amounts to 0.16 percent. This difference is undoubtedly attributable to the fact that in the calculations made from the Harvard data, no account was taken of the water equivalent of the small portion of the glass vaporizer which dipped into the calorimeter water. Assuming that this was about two grams, which is a likely figure as the vaporizer was not set quite as

¹ The correctness of this graph was determined by the method of least squares. Since the curve is linear the equation used was of the form

$$S = \frac{(\sum x \cdot \sum xy) - (\sum y \cdot \sum x^2)}{(\sum x)^2 - n \sum x^2}.$$

TABLE V

Number of run	Weight of water condensed (<i>vacuo</i>)	Time in minutes	Time for one gram	Rise of temperature (corrected)	Total water equivalent (<i>vacuo</i>)	Barometric pressure	Temperature of steam (T°)	Mean temperature of cal- orimeter (t°)	Heat evolved by cooling one gram of water	Heat of vaporization + heat evolved by cooling	Heat of vaporization of one gram at T°	Correction to reduce to 100°	Heat of vaporization of one gram at 100°
7	10.172	9.25	0.910	4.726	1325.9	734.8	99.06	20.41	78.74	616.01	537.27	-0.59	536.7
10	8.201	8.0	0.977	3.811	1324.9	731.0	98.91	20.85	78.15	615.69	537.54	-0.69	536.8
12	8.611	6.0	0.697	4.004	1325.1	724.5	98.67	21.12	77.64	616.16	538.52	-0.82	537.7
13	8.899	5.0	0.562	4.145	1325.5	724.5	98.67	20.22	78.54	617.38	538.84	-0.82	538.0
14	8.933	4.0	0.448	4.163	1325.3	725.0	98.69	20.30	78.48	617.63	539.15	-0.82	538.3
16	8.982	12.0	1.337	4.165	1325.3	728.4	98.82	20.67	78.24	614.57	536.33	-0.74	535.6
17	8.744	11.0	1.259	4.062	1325.2	738.5	99.20	20.14	79.15	615.61	536.46	-0.50	536.0
18	8.598	13.0	1.513	3.989	1325.1	737.8	99.17	20.53	78.73	614.47	535.74	-0.54	535.2
19	9.687	7.0	0.723	4.510	1325.7	736.0	99.10	20.16	79.03	617.20	538.17	-0.57	537.6
21	9.689	10.0	1.033	4.500	1325.7	747.8	99.55	20.14	78.90	615.70	536.80	-0.28	536.5
23	9.301	4.0	0.430	4.337	1325.5	732.9	99.14	20.10	78.98	618.07	539.09	-0.63	538.5
24	9.122	9.0	0.988	4.237	1325.4	—	99.14	20.70	78.53	615.63	537.10	-0.54	536.6
27	9.528	10.0	1.050	4.428	1325.6	—	99.09	20.23	78.95	616.05	537.10	-0.57	536.5
29	9.612	12.0	1.249	4.459	1325.6	—	99.07	20.42	78.74	614.95	536.21	-0.59	535.6
30	10.507	14.0	1.334	4.867	1326.1	—	99.01	20.34	78.76	614.25	535.49	-0.57	534.9
31	9.734	8.0	0.823	4.522	1325.7	—	98.85	20.58	78.36	615.85	537.49	-0.72	536.8
33	9.498	10.0	1.054	4.413	1325.6	—	98.13	20.48	78.74	615.90	537.26	-0.55	536.7
36	10.103	13.0	1.288	4.681	1325.9	—	98.85	20.60	78.34	614.33	535.99	-0.72	535.3
37	9.911	14.0	1.414	4.596	1325.8	—	98.87	20.18	78.78	614.81	536.03	-0.71	535.3
39	8.387	4.0	0.478	3.909	1325.0	—	99.02	20.73	78.38	617.55	539.17	-0.63	538.5
41	7.858	13.0	1.656	3.639	1324.7	—	98.88	20.82	78.15	613.47	535.32	-0.71	534.6

Mean, 20.5

low as in the new series (in which it will be remembered that the correction for the quartz was 4.2 grams), the Harvard series would have given the same value as that found in this new series.

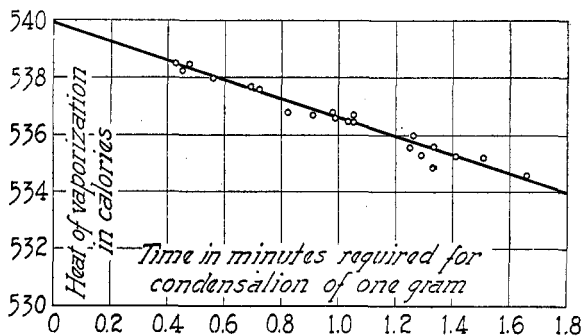


Fig. 4

The value obtained in the new series is slightly higher than that obtained by Henning, whose electrical method worked out at the Reichsanstalt is probably the best of its class. Henning's value for the heat of vaporization of a true gram of water at 100° is 538.7 cal._{15°}. Inasmuch as the two methods are quite different in principle, one depending on a measurement of the energy required to vaporize a gram of water, while the other depends on the measurement of the energy given out by the condensation of a gram of vapor, the agreement of the two methods, each of which is the most refined of its class, indicates that the true value for the heat of vaporization of a gram of water at 100° has about been reached.

Summary

1. The method devised by Richards and the writer for the determination of the heats of vaporization of liquids has been improved upon, particularly by the substitution of a vaporizer made of transparent quartz for those made of glass; and by the use of a better type of adiabatic calorimeter.
2. The water equivalent of the calorimetric system has been determined with accuracy.

3. The amount of heat required to vaporize a true gram of water into a vacuum at 100° has been ascertained to be 539.0 cal_{s.15°}.¹

¹ If the value for the water equivalent of the apparatus as determined by the electrical method be used in the calculations, the value for the heat of vaporization is raised exactly one calorie. On this basis, which may be more nearly correct than the other on account of the uncertainty of the exact specific heats at 20° of the substances composing the calorimetric parts, the heat of vaporization of a true gram of water at 100° is 540.0 cal_{s.15°}. This agrees well with the value obtained by Smith, which was 540.7.