rium. This is perhaps the first observation of this type of phenomenon.

7. The temperature of the decahydrate-hexahydrate transition is found to be approximately 19.525°, on the international hydrogen scale.

8. The temperature of the decahydrate-tetrahydrate transition is found to be approximately 19.987 on this scale.

9. The temperature of the hexahydrate-tetrahydrate transition is found to be approximately 25.90°, on this scale.

10. All these points, especially the last, are to receive further investigation at Harvard in the near future.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]
INVESTIGATIONS ON LIGHT AND HEAT PUBLISHED WITH AID FROM THE RUMFORD FUND.

A METHOD FOR DETERMINING HEAT OF EVAPORATION AS APPLIED TO WATER.

BY THEODORE W. RICHARDS AND J. HOWARD MATHEWS.

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Among usual calorimetric measurements none has been in the past less satisfactory than the measurement of heat of vaporization. The methods employed have been almost as untrustworthy as they have been numerous. The results for water are indeed not very divergent, but in most other cases there is little or no concordance. In the case of ethyl formate, for example, the variation in the values given by different experimenters is over 10 per cent.; in the case of ethyl acetate, the extreme difference is over 13 per cent. These cases have been selected because they concern substances carefully investigated by many observers; less carefully studied cases might have been selected which show even greater discrepancies. Evidently most of the results are in error: but which are the correct ones? The newest values are by no means necessarily the best, for wide discrepancies have appeared in the most recent work. Part of the errors were undoubtedly due to impurity in the materials, and some to faults in the methods.

Desiring really to know the heats of evaporation of a few liquids, we felt hopeless concerning our ability to select among these discordant figures. New research was evidently needed, involving great care in purification of material, and careful choice of the best details of experimentation. The present paper contains an account of the evolution of a satisfactory method.

A brief account of previous methods may well precede the description of our own experimental work, as this was based partly on the successes and partly on the failures of others.

The methods used for measurements of heats of evaporation are of two classes. In one the energy used in the process of vaporization is measured; in the other the energy given up by the condensation of vapor is evaluated; each procedure should of course yield the same results. Most of the methods used, particularly the earlier ones, belong to the latter class; because, although those belonging to the first class have the advantage of being independent of the values for the specific heats of the substances used, they are more complicated in manipulation and calculation, and none has proved to be entirely satisfactory.

Joseph Black[1] was the first to make the interesting observation, that in the formation of the vapor phase from the liquid phase heat is absorbed. His first experiments, though extremely crude, were sufficient to show that in the case of water the amount of heat absorbed by this transformation is considerable. Somwhat later Black and Irvin made further experiments in this direction, and found the value 520 calories per gram, which is surprizingly close to the now generally accepted value, considering the crude method with which they worked. In 1781 Watt[2] for a short time attacked the subject at the suggestion of Black, and about fifteen years later returned to it and made a number of measurements, the details and results of which he published. He pointed out that heat is lost through radiation, but found no method of measuring this loss. He showed also that the condenser gains heat by conduction when connected directly to the boiler by means of a metallic tube, and sought to overcome this source of error through making the connection by means of a cork, so that metallic contact was avoided. The average of eleven separate determinations gave him the value 525.2 calories, or 625.2 from zero,[3] the values varying from 612.9 to 637.1, a difference of about four per cent.; but he expressed his opinion that the true value is not far from 633 calories.

Somewhat later Count Rumford[4] made three experiments concerning the same constant, finding the mean value 667 as the total heat of evaporation from zero—a result much higher than Watts'. Rumford also determined the heat of evaporation of two or three organic liquids, but these results have no value, since, as he admits, the substances were not pure. In this work he sought to overcome the error due to radiation by starting a determination with the calorimeter water at a temperature as much below the surrounding temperature as it would be above it at the completion of the determination, on the assumption that the gain in heat during the first half of the total time would be exactly counterbalanced by the loss in the second half. This practice has

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[1] See Regnault's Experiences, Part I, p. 635 (1847).

[2] Regnault, *Mém. de l'Inst. de France*, 21, 635 (1847); Robinson's, *Mechanical Philosophy*, 2, 5 (1822).

[3] This latter number includes the heat necessary to raise the gram of water from 0° to 100°.

[4] See Biot's, *Traité de Physique*, 4, p. 710.

recently been found to be of very doubtful advantage.[1] In 1818 Ure[2] found the value 637.5 calories; and Despretz,[3] in 1823, published the value 631 as the result of one series of measurements, and 640 as the result of a second series, his apparatus having been similar to that used by Rumford. The next work was done by Brix[4] in 1842, who pointed out many of the causes of error and sought to correct them mathematically. His value for water was 640, including the heat given up by the water between 100° and 0°—a result very close to the most probable figure.

In 1847 Regnault[5] published his exhaustive memoir upon this subject, which surpassed in detailed precaution any preceding work. As an average of 38 separate determinations he obtained the value 636.67 calories, the individual values varying between 635.6 and 638.4.

The work of Andrews[6] may be considered somewhat more in detail, because his method was similar to those which have since been usually employed. He distilled the liquid from a screened retort into a spiral condenser placed in a calorimeter, and noted the rise in temperature. The water equivalent of his calorimeter, water, and utensils was only about 280 grams, the amount of water distilled was a little less than two grams, and there was no device to prevent particles of water from being carried over in the vapor, so that the method was still evidently in its infancy. His thermometric precautions and his efforts to apply corrections for heat lost and gained by radiation were very crude, as was also his method for determining specific heats; but nevertheless, for alcohol, he obtained 202.4 at the boiling point, a value which is but 3 per cent. lower than the present accepted value. His two figures for water, 531 and 543 calories (not including the heat required to warm the water), obtained at different rates, were less satisfactory; premature condensation evidently took place in his apparatus.

Favre and Silbermann[7] shortly afterwards measured th heats of vaporization of a number of organic liquids as well as of water, but the amount of material used was very small and the method in general unsatisfactory, so that their results are of but doubtful value.

The next work of importance is that of Berthelot,[8] whose method (a modification of Andrews') is so well known as to need no description. The vaporizer was placed immediately over the calorimeter and heated by a ring burner, the tube for delivering the vapor passing through

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[1] T. W. Richards and L. L. Burgess, THIS JOURNAL, 32, 449 (1910).

[2] Ure, *Phil. Trans.*, 1818, 385.

[3] Despretz, *Ann. chim. phys.*, [2] 24, 323 (1823).

[4] Brix, *Pogg. Ann.*, 55, 341 (1842).

[5] Regnault, *Mém de l'Inst. de France*, 21, 638.

[6] Andrews, *Pogg. Ann.*, 75, 501 (1848).

[7] Favre and Silbermann, *Ann. chim. phys.*, [3] 37, 461 (1853).

[8] Berthelot, *C. R.*, 85, 646.

the ring. His apparatus, although ingenious, has grave defects, some of which have been pointed out by Schiff[1] and by Kahlenberg.[2] Superheating of the vapor, the most glaring defect, was suspected by the former critic, but the experimental demonstration was first made by the latter. Another source of error is direct radiation from the burner into the calorimeter, for which, however, an approximate although unsatisfactory correction may be applied. There was no device to prevent the vapor which came off from the liquid before it reached the boiling point from gaining access to the condenser.

Passing over the work of Schall,[3] who used the method of Favre and Silbermann, we come to the work of Robert Schiff,[4] who sought to avoid the causes for error in the Berthelot apparatus by removing the source of heat from the neighborhood of the calorimeter, and interposing a small silver trap just before the entrance of the vapor into the condenser. By this ingenious device, particles of unvaporized material that might be carried over by the current of vapor, and most of the liquid resulting from a premature condensation of the vapor, would be caught and prevented from going into the condenser. Some of the earlier experimenters had sought to prevent prematurely condensed liquid from reaching the condenser by making a sharp bend in the vapor delivery tube, so that condensed liquid would run back into the vaporizer, but Schiff's device has the decided advantage that the trap can be placed much closer to the condenser, so that the amount of condensation between this point and the condenser will be smaller. That this was a distinct improvement is apparent in his results; they were among the best that have been made. While the method of Schiff is undoubtedly better than any similar methods previously used, it is objectionable in the case of liquids of higher boiling point, as Kahlenberg has shown. The danger here arises from the fact that a substance of high boiling point condenses in the trap to such an extent that it finally overflows and runs into the condenser.

Another objection, heretofore not mentioned, lies in the fact that the vapor, just before it reaches the calorimeter, passes through a zone, which, though heated, is not quite as high in temperature as the boiling point, and consequently premature condensation is not wholly avoided. By no means all of the heat thus lost finds its way into the calorimeter. The result of this defect is to give a value lower than the true heat of vaporization.

In the hands of Louguinine[5] the apparatus of Schiff has been so perfected as to make it one of the most satisfactory heretofore used. The

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[1] Schiff, *Ann.*, 234, 338 (1886).

[2] Kahlenberg, *J. Physic. Chem.*, 5, 215 (1895).

[3] Schall, *Ber.*, 17, 2199 (1884).

[4] Schiff, *Loc. cit.*

[5] *Ann. chim. phys.*, [7] 7, 251 (1896).

tube leading to the trap was made large in order to prevent the clogging with condensed liquid. The proximity of the hot trap to the calorimeter necessitated a correction for heat gained therefrom through radiation and conduction. In Schiff's work this correction appears to have been omitted, but Louguinine evaluated this cause of error by keeping the trap hot while he prevented both vapor and liquid from entering the condenser. In this way the heat gained per minute by radiation and conduction can be determined fairly well, and, knowing the time during which vapor enters the condenser and gives up heat, a suitable correction can be made for the heat gained by radiation and conduction during the same period. Louguinine made the distance from the trap to the condenser very short (15 mm.) in order to reduce the premature condensation of the vapor, but our experience indicates that even then he could not have been wholly successful. The fact that his results for the heat of vaporization of water are fairly concordant does not prove the absence of error from this cause. To reduce condensation to zero, the distance between trap and condenser should also be reduced to zero—an obvious impossibility. Because, as has been said, the effect of the error is to make the heat of vaporization appear less than it really is, Louguinine's three values, 535.61, 537.61 and 538.51 calories per gram, are probably too low.

About fourteen years ago J. A. Harker[1] published an elaborate and interesting account of his work. His early rejected experiments demonstrated more conclusively than ever the danger of premature condensation, and he concluded that this cause of error is inevitable, when the vapor is introduced from above. In his later work, fearing that minute drops of water exist in vapor as ordinarily formed in distillation, he passed the vapor through coils in a heated oven, and then through a zone kept at a constant temperature about three degrees above the boiling point. Finally the vapor was admitted into the condensing coil of the calorimeter, through the side of the latter, the temperature being taken at the point of introduction by means of a calibrated thermo-couple. The apparatus was ingenious, but the conduction of heat into the calorimeter from the entering tube must have been considerable, and heat was undoubtedly gained also by direct radiation from the black interior surface of the ebonite chamber at the opening in the side of the calorimeter.

He concluded from his experiments, which he wished to be considered as merely preliminary, that the true value for the heat of vaporization of water (not including the heat given out in cooling the water) is about 540 calories. Unfortunately, his data, corrections and calculations are not given.

Kahlenberg,[2] in an almost simultaneous investigation, sought to re-

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[1] Mem. Manchester, *Lit. and Phil. Soc.*, [4] 10, 38 (1896).

[2] Kahlenberg, *J. Physic. Chem.*, 5, 215 (1895).

tain all the good qualities of the method of Berthelot, and at the same time endeavored to eliminate its sources of error by an ingenious modification, using the heat generated from an electric current conveyed by a resistance wire immersed under the liquid to be vaporized, in order to produce the vaporization. Thus superheating is avoided, as well as the presence of any flame near the calorimeter. This method, undoubtedly one of the best heretofore used, has yielded fairly good results, which are nevertheless undoubtedly somewhat vitiated by premature condensation.

Other methods which should be considered are the electrical methods of Marshall and Griffiths,[1] of Marshall and Ramsay,[2] of Brown,[3] and of Henning.[4]

The method of Marshall and Griffiths is exceedingly complicated, and the heat of vaporization of but one substance, benzene, has been obtained. The values werē determined for the temperatures of 50°, 40°, 30° and 20°, and the value at the boiling point obtained by extrapolation. Upon this value for benzene, thus obtained, was based all the work done by Marshall and Ramsay. This latter method was merely a comparative method. The electric current was sent through two similar vaporizers in series, and the amount of liquid distilled from each was weighed. The results obtained all depended, therefore, upon the value of the heat of vaporization of one substance, and for this one substance different experimenters had found values differing by over sixteen per cent. The investigators state that they were unable to obtain any satisfactory results for water, perhaps because of electrolysis and its consequent consumption of electrical energy.

Brown, working with a single apparatus, passed a current of measured value for a measured time through a wire of known resistance, immersed under the liquid. The portion evaporated was weighed; thus all the data for calculating the heat of evaporation were obtained. As in Ramsay's and Marshall's method the liquid must be at the boiling point before the measured current is passed through, but no knowledge of the specific heat of the liquid is necessary. The results obtained by Brown agree well among themselves, but are even higher in value than those obtained by Marshall and Ramsay.

F. Henning[5] used a method similar in principle to that used by Brown, but superior in detail, because greater precautions were taken to provide against possible errors. The original paper must be consulted for

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[1] Marshall and Griffiths, *Phil. Mag.*, [5] 41, 1 (1896).

[2] Marshall and Ramsay, *Ibid.*, [5] 41, 38 (1896).

[3] Brown, *J. Chem. Soc.*, 83, 987 (1903).

[4] Henning, *Ann. Physik*, [4] 21, 849 (1906).

[5] *Loc. cit.*

particulars, most of which do not immediately concern the present investigation. The greatest difficulty in this interesting and painstaking work seems to have been that considerable heat was necessarily carried away by the conducting wires, and there seems to have been no entirely satisfactory method for measuring or calculating this uncertain quantity. As the mean of his determinations made at an average temperature of 100.59°, Henning found the heat of vaporization of a gram (weighed in vacuum) of water to be 538.25 calories at 15°. A number of determinations were made also at reduced pressures, but they do not concern us here.

A modification of this electrical method has been proposed by A. Cameron Smith,[1] who suggested that the electrically heated vaporizer be suspended from one arm of an analytical balance. This apparatus is suitable only for lecture demonstrations; many possible sources of error tend to diminish its accuracy.

Among these many methods, Kahlenberg's modification of Berthelot's seemed to be preferable, partly because of its simplicity, and partly because it retains the advantage of the electrical method of heating while avoiding the disadvantages. Hence we used this method as the basis of our own, seeking to discover and correct any sources of error which might still remain in it.

The Evolution of the Present Apparatus.

One of the most serious causes of error in all calorimetric work is the more or less uncertain correction for cooling. Hence one of the first steps of the present research was the application of the new method of adiabatic calorimetry to the problem.[2] This method, first put into practice about six years ago at Harvard, has since been used successfully in several calorimetric processes, such as the determination of specific heats of neutralization, combustion, and solution. The method consists in warming the

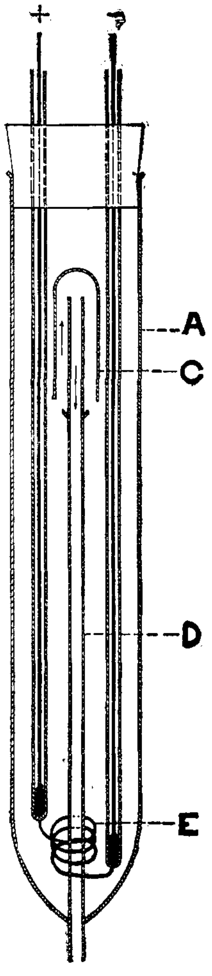

Fig. 1.—First modification of Kahlenberg's vaporizer.

The hood or trap (C) over the delivery tube helps to eliminate mechanically carried drops.

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[1] *Proc. Roy. Soc.*, Edinburgh, 24, 450 (1903).

[2] Richards, Forbes and Henderson, *Proc. Am. Acad.*, 41, 1 (1905). See also Richards and Jesse, as well as Richards and Burgess, THIS JOURNAL, **32**, 268 (1910) and 32, 431 (1910).

surroundings of the calorimeter at the same rate and to the same extent as the calorimeter itself during its operation. This is accomplished by surrounding the calorimeter proper by a water-tight jacket, which is immersed in a larger vessel containing dilute alkali. Into the latter can be delivered the requisit amount of acid, the bath being stirred rapidly so as to insure uniformity of temperature. By such a system it is possible to prevent heat exchange to or from the calorimeter proper, and the thermometer is stationary during both the initial and the final readings.

For the measurements of the heat of vaporization a modified form of Kahlenberg's apparatus was combined with the adiabatic method of calorimetry. The exact form of apparatus finally used was reached only by degrees, several successive improvements having been introduced. The first modification of Kahlenberg's vaporizer consisted in the interposition of a trap or hood (C in Figs. 1, 3, 4 and 5) between the boiling liquid and the condenser, to prevent drops of unvaporized material from being carried into the latter by the lively current of vapor. The objection to such a trap as that used by Schiff (namely, premature condensation of vapor) was avoided by keeping the trap entirely enclosed by the vapor of the boiling liquid, and therefore at the same temperature. Furthermore it was made in such a form as to prevent any danger of its filling and running over.

With this apparatus a number of preliminary determinations were made, with a condenser and calorimeter to be described presently, and a striking systematic irregularity was observed in the results. The heat of vaporization of benzene, for example, appeared to be about 89 calories when 25 grams took 14 minutes to evaporate, but as much as 93 calories when the time was shortened to 2.5 minutes, with corresponding results for intervening rates. The results are plotted in the accompanying diagram.

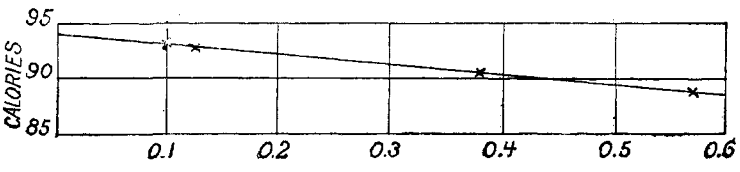

Fig. 2.—The effect of speed of vaporization on the results. (Benzene in the vaporizer shown in Fig. 1.)

In the direction of ordinates are plotted the observed values for the heat of vaporization of a gram of benzol in small calories; in the direction of abscissas are plotted the times (in fractions of a minute) needed for the vaporization of that quantity.

The ordinates represent heats of vaporization in calories, and the abscissas the time in minutes required to vaporize one gram. By a comparatively short linear extrapolation we obtain the value 94.1 cal. as the heat of vaporization of benzene. It will be shown in a subsequent paper that this value is very near the most probable value obtained afterwards with better apparatus. Water was found to exhibit precisely the same phenomenon. Previous investigators have not taken into consideration this variation of result produced by varying the rate of distillation, and the oversight undoubtedly accounts for much of the wide variation in the published results.

Consideration of the various possible complications which might bring about this time effect led to the conclusion that it was probably due to premature condensation between the vaporizer and the condensing coil, and the consequent loss of heat from the vapor thus condensed. Evidently such a loss must be directly proportional to the time required for the vapor to pass through the zone of premature condensation. Further, in accordance with Newton's Law of Cooling, the loss of heat should be proportional to the difference in temperature between the boiling point of the substance and the environment of this zone—a conclusion later verified by the facts.

Attempts were next made to eliminate as far as possible the zone of premature condensation. The vaporizer was set into an asbestos shield made n the form of a frustrum of a cone, the space between the asbestos and the glass being closely packed with cotton, and the outside of the cone covered with bright tinfoil to cut down the radiation. In order to place the vaporizer as low as possible and at the same time to prevent its becoming wetted, a shallow glass cup was placed immediately below the asbestos shield. The cup also served to prevent loss of heat by evaporation of the calorimeter water at its surface, or by evaporation of water rising on the vaporizer stem by capillary action or other cause, such evaporation being caused by the presence of the hot tube carrying the vapor. In this manner the distance between the boiling liquid within the vaporizer and the calorimeter water was reduced to a little less than one centimeter.

In spite of the precautions to prevent radiation, the correction for heat gained by the calorimeter due to this cause was increased from about 0.002° to 0.008° per minute, a quantity which was very carefully determined and applied to the results.

This vaporizer yielded results which gave when plotted a line less steep than the previous one. The modification had evidently improved the results, but had not wholly eliminated the cause or causes of error.

In the space above a boiling liquid in a flask, a mist can often be observed. This mist is caused by radiation of heat from the walls of the vessel; and the question arose as to whether the difficulty in obtaining uniform results at various speeds might not be due in part to the formation of such a mist within the vaporizer. The mist would not be entirely caught by the trap, and would thus introduce minute drops of water into the condenser, possibly proportional in amount to the time required for distillation.

In order to discover whether any difficulty arose from this cause, the vaporizer, above the asbestos cone, was surrounded by a jacket through which live steam was passed throughout the measurement. This must have prevented the formation of a mist within the vaporizer, but the results were no better.

The ejection of fine drops from the surface of the boiling liquid—drops which might be swept along by the current of vapor—could not have been the cause of the particular trouble in question. Such an action would seem more likely when the boiling is rapid than when it is slow, an outcome exactly the opposit to that actually observed. Doubtless such an ejection occurs to a slight extent, but in our trap its effect had undoubtedly been much reduced. As will be seen, our final result shows that we have been at least as fortunate as others in eliminating this danger.

Harker, in his desperation on account of obvious premature condensation, resorted to superheating the vapor, in order to insure its being perfectly dry; accordingly we, too, tested this doubtful device. A coil of fine platinum wire was introduced into our vapor delivery tube, extending nearly its whole length, and a small current was sent through the wire. Several determinations made at different speeds and with different strengths of current through the coil, gave higher values than before. With a constant strength of current, the slower the speed the higher was the result; and with a constant rate of evaporation, the greater the current the higher was the result. Evidently superheating occurred. With some modifications of the parts and the construction of special thermometers it would have been possible to take the temperature of the vapor as it entered the calorimeter; but the unsatisfactory nature of these experiments offered no temptation to the further prosecution of this line of attack.

Being still convinced that the principal premature condensation took place in the narrow zone between the vaporizer and the condenser, we next sought to reduce further this distance, and to protect the vapor passing through it from loss of heat. A new vaporizer having a vacuum jacket was constructed as shown in Fig. 3, the walls (B) of the jacket being about one centimeter from the walls (A) of the vaporizer, save at the bottom where the distance was about eight millimeters. Both the outer wall of the vaporizer and the inner wall of the jacket were brightly silvered to a distance of about five centimeters above the vapor exit. The vaporizer was set so low that the level (F) of the calorimeter water came up on its jacket to a height of a few millimeters. This brought the boiling liquid in the vaporizer to within one centimeter of the calorimeter water, largely protected the vapor from condensation in this zone, and prevented most of the evaporation from the surface of the calorimeter water at the line of immersion. The vaporizer projected a short distance through the adiabatic cover, and, since the projecting part was silvered, the amount of radiation was not excessively large. The space around the vaporizer was closely packed with cotton. With this apparatus, values were obtained which were slightly higher than those previously obtained with the earlier forms of apparatus, when made at the same rate; but they were not as consistent as desired, partly because of the fact that the diameter of the exit of the delivery tube was much too large.

Another attempt to reach a better result led to the cutting off of still more of the delivery tube below, the thermal protection being provided only by a rubber cup, cut from a child's ball, placed between the vaporizer and condenser. The rubber cup was packed with cotton, as was also the space around the vaporizer. After a few determinations, however, the apparatus was discarded, because the correction for radiation and conduction was very large (0.040° per minute), and also because of the difficulty in making a tight joint.

The form of apparatus finally adopted combined all the advantages of the preceding forms, and is shown in Fig. 4. The boiling liquid was surrounded by a vacuum jacket whose walls were about one centimeter from the walls of the boiling compartment, save at the bottom where the space was five millimeters across. In addition to the hood covering the upper end of the vapor delivery tube, the tube was also provided with another trap to catch and retain any liquid that might in any way gain access thereto. This trap

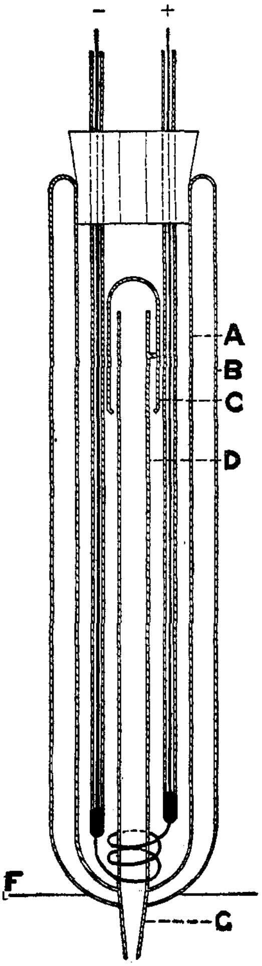

Fig. 3.—A further modification of Kahlenberg's vaporizer.

The compartment containing the liquid and coiled platinum wire for heating is surrounded by a silvered vacuum jacket (AB). The trap (C) is retained. The condenser is attached at G. The vaporizer is immersed in the water of the calorimeter as far as the water-line at F.

was placed as low as possible so that the distance between it and the condenser might be reduced to a minimum, yet it was surrounded by the boiling liquid in order to prevent condensation within it. The heating coil was placed so low as to make sure that the liquid surrounding the trap was at the boiling point. If prematurely condensed liquid now gains access to the condenser, it must come entirely from condensation in the short distance between the trap and the calorimeter water, —because all previously condensed liquid was caught in the trap. After an experiment the trap usually contained a few drops of liquid, sufficient to have introduced appreciable error, had it been allowed to reach the condenser.

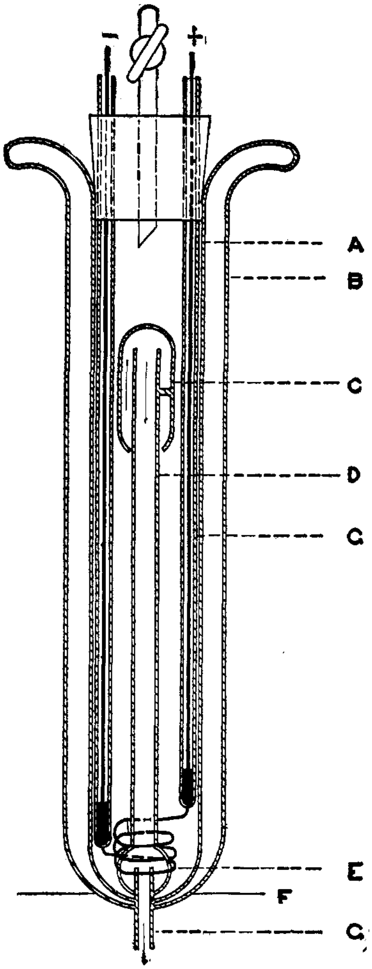

Fig. 4.—Final form of vaporizer (½ actual size).

A vacuum jacket (AB), silvered inside, surrounds the hot vessel, which is provided with a stopcock above. The delivery tube has two traps, one over its top (C), and another (E) as near as possible to the water of the calorimeter below. The condenser is attached at the very bottom at G, and F is the water-line, as in Fig. 3.

The interior of the vacuum jacket was brightly silvered to a height of 4 or 5 centimeters, the silvering being on both walls, so that any heat passing from the boiling liquid to the calorimeter water by radiation had to pass through two brightly silvered surfaces and a vacuum space. The conduction of heat to the calorimeter through the glass itself cannot be prevented, but was made small by having the glass as light as was consistent with the strength demanded. The proper correction was always applied for heat gained by the calorimeter in these two ways, the necessary observations being always determined before each measurement of latent heat. For several minutes previous to admitting the vapor into the condenser, readings of the temperature were made at intervals of one minute, until the increase became constant and of certain value. The nature of the problem is such as to make this correction absolutely necessary, for the vaporizer must be brought close to the calorimeter water, and radiation and conduction across this small distance cannot be prevented.

After many experiments had been made, not only with water but also with higher-boiling substances, the accidental cracking of the vaporizer jacket near the top destroyed its high vacuum; nevertheless the correction for the combined radiation and conduction was then found to be but little greater than before. Apparently the two brightly silvered surfaces effectually prevented radiation.

The heating coil had a resistance of about 0.7 ohm, and was supplied with a suitably controlled current of from twelve to eighteen amperes from eight large storage cells. The ends of the coil were sealed into the ends of small glass tubes within which were stout copper wires, contact being made by mercury. It is necessary that the copper wires be heavy so that they may not become heated, and thus superheat the vapor coming into contact with the glass tubes encasing them.

The temperatures at which distillations took place were read from small standardized Anschütz thermometers, whose mercury threads were entirely within the vapor, so that no correction for projecting mercury thread was necessary. The bulb of the thermometer was placed opposit the entrance to the hood, in order to measure the temperature of the vapor actually admitted—a point especially emphasized by Louguinine, who nevertheless merely inferred the temperature from the barometric pressure and the coefficients expressing the dependence of boiling point on pressure.

Another point, usually neglected, is worthy of brief notice. Before the liquid comes to the boiling point, an appreciable quantity of vapor may pass over and be condensed. Obviously this may introduce error, since the assumption is made, in calculating the result, that all the vapor was at the boiling point of the liquid. Moreover, the heat of vaporization is different at different temperatures. In the present experiments this cause of error was eliminated by providing the vaporizer with an outlet and stopcock above, and by passing a very slow current of dried air backwards through the condenser coil and vaporizer until the liquid was boiling at a lively rate, and the temperature of the whole interior was quite at the boiling point of the liquid. This air prevented the vapor from passing into the condenser, so that no premature condensation was possible; its initial temperature was kept close to that of the calorimeter.

Preliminary experiments were made to find whether or not the proximity of the hot coil of platinum wire might superheat the vapor passing in its downward course to the condenser. The wire was first made into a coil about 3 cm. in diameter, and a thermometer suspended therein, the bulb of the thermometer being at the center. The coil and thermometer bulb were then immersed in distilled water in a large open test tube, the current was connected, and the temperature noted at which boiling occurred. The coil was then made about 2 cm. in diameter and the process repeated; finally the wire was coiled as tightly as possible around the thermometer bulb, without actual contact, and the temperature at which boiling took place was noted as before. It was found that there was no danger of superheating from this source, as the temperature recorded by the thermometer was exactly the same in all three cases. As long as the wire is covered with liquid, it matters not whether the resistance wire is coiled loosely or closely around the tube through which the vapor is passing. Hence vapor passing through a tube similarly encircled by hot wire must be free from superheating.

The calorimeter, of about 1.5 liters capacity, was made of thin nickel-plated sheet copper, highly burnished on the outside. It was almost filled with water, and is shown in Fig. 5 (D, D). The condenser (A) within the calorimeter was constructed of block tin, the joints being soldered by tin only; it consisted of a spiral tube, 1 meter long and 3 millimeters in internal diameter, coiled in four turns, with a tin cylinder 10 centimeters long and 3 centimeters in diameter at the bottom to serve as a receptacle for the condensed liquid. The tin cylinder had an outlet tube, leading directly up to the air of the room. The tin coil and cylinder together weighed 436.7 grams. The outlet tube or break of the vaporizer was attached to the worm by a short piece of pure rubber tubing (B). Various preliminary experiments were made as to the position of this joint in relation to the water of the calorimeter, but the details need not be given. Finally, the arrangements shown in the figure was adopted; the silvered jacket of the vaporizer was immersed to the depth of about a centimeter under the water. The water-line was thus protected from heat by the vacuum jacket, and abnormal evaporation and cooling at this point were therefore avoided.

The stirrer (C) within the calorimeter was of the propeller pattern, having six blades, each 1 centimeter long. It was made of copper, and, in order to prevent loss of heat by conduction, extended only to the surface of the water, where it joined a shaft of hard rubber to which was attached the driving mechanism. The scarcely perceptible evolution of heat from the stirrer, being directly proportional to the time of the experiment, was included with the warming due to the proximity of the vaporizer in a single time correction, and thus eliminated from the result.

The heat capacity of the solid parts of the calorimeter was equivalent to 53.4 grams of water, the separate parts amounting to the following quantities. The finished copper calorimetric vessel weighed 299.95 grams. It was "plated" inside and out with a thin electrolytic film of burnished nickel, which has a specific heat so near that of copper as to cause no appreciable difference in the heat capacity of the whole. The copper vessel was soldered with about 4 grams of solder, the solder consisting half of lead and half of tin, and having therefore a specific heat of about half that of copper. The calorimeter vessel with its nickel and solder was therefore approximately equivalent to the pure copper vessel, weighing 298 grams, and had a heat capacity equivalent to 27.7 grams of water, the specific heat of copper at 21° being about 0.093. It may be noted that the weight of the copper vessel need not be known within two or three grams, for this corresponds to the limit of possible

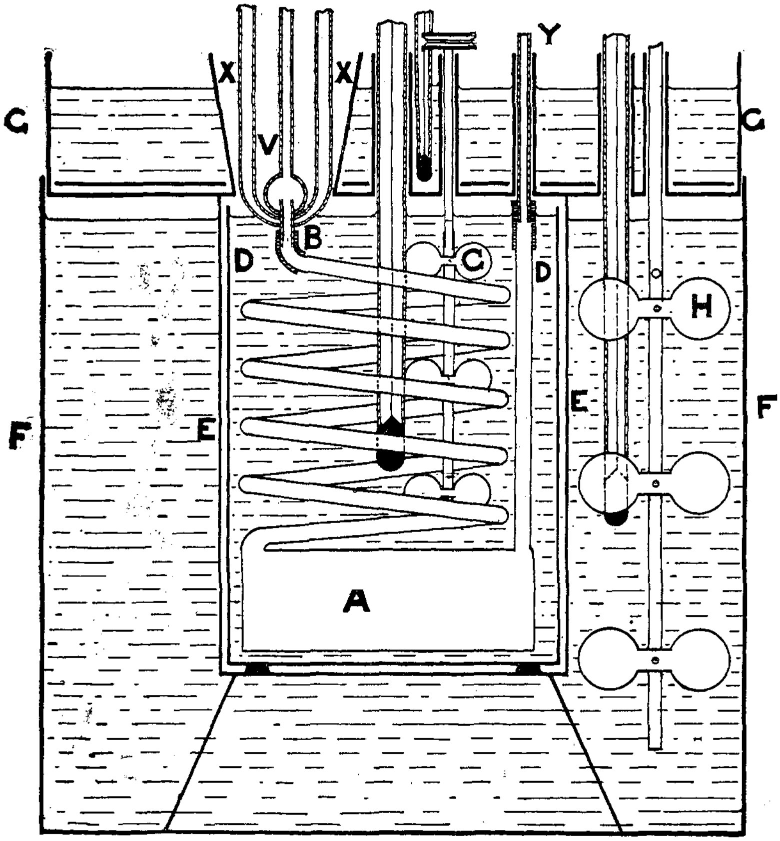

Fig. 5.—The calorimeter. The vaporizer (V) is set within a large hole (XX) in the cover. At B is attached the condenser A immersed in water contained in the calorimeter. Between the jacketing vessels E and F is dilute alkali, into which sulfuric acid is dropped in order that the temperature of the surroundings should keep pace with that of the calorimeter proper. C is a stirrer within the calorimeter, H one in the outside vessel.

accuracy of the thermometric part of the experimentation. The pure tin condenser weighed 436.7 grams, and therefore had a heat capacity equivalent to 23.6 grams of water, the specific heat of tin at 21° being about 0.054.[1] The thermometer was found by the method of Ostwald-Luther[2] to have a heat capacity equivalent to 1.4 grams of water; and the copper stirrer, weighing 7.7 grams, had a heat capacity of 0.7 on the same basis. These weights have as their sum 53.4 grams.

An important matter of detail lay in the discovery of the time needed for equalization of temperature between the hot liquid accumulating in the condenser and the water of the calorimeter. In order to test this, a glass funnel was substituted for the vaporizer at B, and 17 grams of water were poured little by little through this funnel during 5 minutes. There being no heated object near the calorimeter, the radiation effect was negligible, and the rise in temperature of the calorimeter water was due only to the hot water introduced.

Immediately after the addition, the reading of the thermometer was a trifle over 1°; in another minute the thermometer read 1.101°; in yet another minute 1.104°. In the 3 minutes following, the thermometer rose 0.001° each minute, and finally remained perfectly constant at 1.107°. Thus in 5 minutes after the last portion of water had been added a constant temperature had been attained, showing that with the rate of stirring usually adopted, this time was sufficient for complete equalization of the temperature within the calorimeter.

The calorimeter was surrounded by a narrow air space, bounded by a copper can (E) with a burnished nickel-plated lining. This was immersed in a much larger vessel (F) of about ten liters capacity, which contained dilute crude sodium hydroxide. The outer vessel was provided with a basin-shaped cover (G) of about 4 liters capacity, through which were several openings for thermometers, vaporizer (V), stirrer, etc. The bottom of the cover was coated with bright tin foil. In this way the calorimeter was entirely surrounded by a uniform temperature, except where the vaporizer protruded through the cover. A powerful stirrer (H), revolving at the rate of 250 revolutions per minute and driven by an electric motor, kept the lower alkaline solution in violent agitation while the solution in the cover was more gently agitated by means of a perforated ring of heavy sheet copper, lifted by an electric motor and allowed to fall by its own weight. The stirring in the cover need not be so energetic as that below, since the temperature in this part of the bath need not be so accurately adjusted as in the lower compartment.

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[1] The specific heats of copper and tin usually given (0.094 and 0.055 respectively) correspond to the range between 20° and 100°. The values given above take account of the decrease with decreasing temperature.

[2] Ostwald-Luther, Handbuch, p. 300 (1910).

As the temperature in the calorimeter rose, because of the condensation of the vaporized liquid, concentrated sulfuric acid was run from burets into both jacketing compartments, so that the environment around the calorimeter was changed in temperature as fast as the calorimeter itself. The details are so similar to those of the other applications of this adiabatic method that they need not be reviewed. The stirring was so effective that the thermometers in different parts of the bath all rose at practically the same rate.

It was found possible to follow the rising temperature of the calorimeter within 0.05° in the lower compartment and within 0.1° in the upper compartment throughout the entire course of the experiment. Suitable tests proved that with so small a difference in temperature there was no danger of appreciable heat exchange with the surroundings during the brief progress of a determination.

The rise in temperature of the calorimeter was measured by a carefully standardized Beckmann thermometer, having a slender bulb and rather a long scale. Readings to 0.001° were made with certainty by means of a lens. The standardization was effected with very great care by comparison with two Baudin thermometers standardized by the Bureau des Poids et Mesures of Paris. The comparison was conducted by immersing all the thermometers in the water of the adiabatic calorimeter surrounded by its jacket. The calorimeter was covered tightly with a non-conducting cover through which the thermometers and stirrer passed, and the thermometer to be studied was immersed to the depth at which it was subsequently to be used. All the thermometers were placed as closely together as possible in order to insure their having the same temperature. The temperature of the calorimeter water could be held perfectly constant for any desired length of time, so that there was no error due to the lag in any of the thermometers. Readings were made (after gently tapping the thermometers) at every $^1/_{10}$° mark, and the corrections were calculated with due account of the correction for the various standardized thermometers used. The Baudin thermometers had previously been found to agree very closely with an accurate Fuess thermometer, which in its turn had been carefully studied by the Reichsanstalt of Berlin.

The various parts of the apparatus having been described in detail, the actual execution of the experimental work may now be considered.

As may have been inferred, many preliminary determinations were made in order to determin the best conditions, and the various dangers to be avoided. Water, having been the liquid most studied by others, was chosen as the most desirable substance with which to test the apparatus and method.

Over thirty trials were made with the object of finding the best position of the vaporizer and testing various devices to prevent radiation.

Finally the following method of experimentation was adopted: The pan-like copper cover (G, Fig. 5) of the calorimeter jacket was placed temporarily upon a raised stand which permitted easy access to its lower surface; the vaporizer (V) containing the liquid to be investigated was adjusted into its place (packing the space X between its silvered envelope and the copper cover with cotton wool) the empty weighed condenser (A) was then attached to the beak of the vaporizer (B) as it protruded beneath the elevated copper cover, and the thermometer and stirrer were arranged in their orifices. Meanwhile the calorimeter had been almost filled with a weighed amount of water as about 20°, and the jacketing crude alkaline solutions had been adjusted at exactly the same temperature. When all was ready, the copper cover with the suspended condenser was placed in position over the calorimeter, the condenser being immersed very carefully in the calorimeter water. The silvered beak of the vaporizer itself dipped about a centimeter under the surface, as shown in the diagram. The slow backward current of air, which served to prevent the access of vapor to the condenser until all was ready, was then driven through the apparatus, and at the same time the heating electrical current was turned on within the vaporizer. When the liquid was actively boiling, a careful study of the radiation-conduction effect on the calorimeter was made. This having been accomplished, the actual experiment could begin; the stopcock (K, Fig. 4) above was closed and the backward current of air discontinued. The rapid current of vapor was thus suddenly switched into the condenser, and the temperature of the calorimeter began to rise at a rapid rate. This rate was continuously matched in the environing alkali by admitting acid in suitable quantities, and the experiment proceeded very smoothly until a rise of about 4 degrees had been accomplished. Finally the stopcock (K, Fig. 4) above the vaporizer was suddenly opened, the posterior outlet (Y, Fig. 5) of the condenser closed, and the electric current cut off. The vapor forming was then free to escape into the air, and when boiling stopped the condensed liquid was not drawn back into the vaporizer by the sudden vacuum formed upon cessation of boiling. For at least five minutes afterwards, the temperature of the calorimeter was read every minute with as great care as at first. After dismounting the apparatus the condensing coil was dried outside and weighed, and the experiment was thus brought to a close.

The increasing temperature and the increasing heat capacity of the calorimetric system during an experiment cause complications in the calculation which have usually received insufficient attention. At the beginning, the heat capacity of the calorimeter is that of the solid-apparatus and the water in which the coil is immersed. As the experiment proceeds, this heat capacity is augmented by the liquid which collects within the condenser. At the end of the distillation the heat capacity of the calorimetric system reaches its maximum. Evidently the value used in the calculation must be taken as the initial heat capacity plus the heat capacity of half the condensed liquid.

Heat is radiated and conducted from the hot vaporizer into the calorimetric system, and correction of this unavoidable complication must be applied. The correction is primarily based upon the measurement of the heat gained during the preliminary minutes before the experiment has been begun, in the usual fashion; but it must be remembered that this value does not apply exactly to the end of the experiment, because the calorimeter has then risen in temperature, and therefore cannot take so much heat from the vaporizer as before. For example, if the temperature of the calorimeter is 20° at first and 24° at the conclusion of the experiment, and if the vaporizer has a temperature of 100°, it is evident that the difference of temperature between the vaporizer and the calorimeter is 80° at first and only 76° at the end. Hence, if the calorimeter gains 0.009° during each preliminary minute, it will be expected to gain only $76/80 \times 0.009° = 0.0085$ during each final minute, and intermediate values during the intervening period. The method of correction for this changing effect is obvious and was easily applied. This practice was justified by the actual results, for the warming effects of the hot vaporizer was always found to be less after the experiment than before. The diminution was manifest even before the vaporizer itself had cooled considerably.

The changing condition of the calorimeter involved a similar detail in the calculation of the heat given out by cooling the condensed liquid from its boiling point to the temperature of the condenser. The heat actually measured in the calorimeter was due, of course, not only to the heat given out by condensation, but also to that given out by the condensed liquid in falling from the temperature of the vaporizer to that of the calorimeter. The first portion of condensed liquid is cooled to the initial temperature of the calorimeter, the last portion only to the somewhat higher final temperature. Obviously here again the mean temperature must be taken in the calculation. Thus, if the experiment began at 20° and ended at 24° and the barometer indicated 760 mm., the first drop of water was cooled through 80°, the last through only 76°. Obviously here again the average value, 78°, should be taken in the calculation. It is easy to show by means of the calculus that all these compromises in the calculation are legitimate.

The amount of water evaporating into the small air space around the calorimeter during an experiment was negligible both in weight and in thermal effect.

There follow, as a typical example, the complete data and computation of a single case, the second given in the table, selected at random from results.

For five minutes preceding the experiment, the calorimeter gained at a perfectly constant rate of 0.009° per minute. When this was certain the vapor was turned into the condensing coil, and after five minutes more the electric current of 14 amperes was stopped, and the vapor prevented from gaining further access to the coil. In yet five minutes the calorimeter had settled down once more to a rate of increase in temperature corresponding to that observed at first, that is to say, 0.0085° per minute, clearly due only to radiation and condensation from the vaporizer. The heat from the actual condensation had all been imparted to the calorimeter, hence the experiment was considered as concluded. The several data and the simple calculation depending upon them are given below. The barometric pressure was exactly 760.0, hence the steam entered the condenser at 100.0°.

In calculating the heat given out in cooling a gram of water from 100° to the mean temperature of the calorimeter (21.42°) the figures of Barnes[1]

Heat of Vaporization of Water.

Determination No. 2.

Time when reading was taken.	Observed thermom. reading in water in calorimeter (uncorrected).	Increase in temperature per minute.
1.21	0.090°	...
1.22	0.098	0.008
1.23	0.107	0.009
1.24	0.116	0.009
1.25	0.125	0.009
1.26	0.134	0.009
1.27	0.143	0.009
1.28	0.152	0.009
1.29	0.161	0.009
1.29	Vapor turned into coil.	Average, 0.009
1.34	Electric current stopped.	
1.35	5.100	...
1.36	5.117	0.017
1.37	5.128	0.009
1.38	5.138	0.010
1.39	5.147[2]	0.009
1.40	5.155	0.008
1.41	5.164	0.009

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[1] Landolt and Börnstein, Tabellen, pp. 393 and 810 (Berlin, 1905).

[2] Point at which rise of temperature due to condensation of vapor ceased. Further increase of temperature, since the rise did not exceed 0.0085° per minute, was due to radiation from vaporizer.

	Reading of thermometer.	Correction to reduce reading to true temperature.	Corrected temperature hydrogen scale.
Final temperature	5.147°	+18.787	23.934°
Initial temperature	0.161°	+18.760	18.921°
Total rise in temperature			=5.013°
Rise due to radiation and conduction (2.5 × 0.009° + 7.5 × 0.0085)			=0.086°
Rise in temperature due solely to condensation of vapor and cooling of resulting liquid to temperature of calorimeter			=4.927°
Water equivalent of calorimeter and fittings			53.4 g.
Water equivalent of water in calorimeter			1252.9
Water equivalent of ½ the liquid condensed			5.26
Total water equivalent			1311.56 g.
Weight of condensing coil and condensed liquid			447.219
Weight of condensing coil alone			436.705
Weight of vapor condensed (liquid vaporized)			10.514 g.

Total heat effect per gram $= \frac{1311.6 \times 4.927}{10.514} =$ 614.63 cals. at 21°.

Heat given out by cooling 1 gram from 100.0°—21.42° = 78.67 cals. at 21°.

Uncorrected heat of vaporization of *one gram* of water = 536.0 cals. at 21°.

were employed, because they probably represent most nearly the present standard of temperature. By graphic integration, the average specific heat of water over this range was found to be 1.0012 times the value at 21.4°; hence is calculated the value 78.67 calories above, corresponding to a fall of 78.58°. The 21° calorie is apparently about 0.9985 times the 15° calorie, hence in terms of the latter the result would be 535.2.

Six determinations were conducted in this way with this vaporizer, two of them being run very slowly and the other with increasing speed. For the slowest about 11 or 12 amperes were usually necessary, and 17 or 18 amperes were required for the fastest. The results are rearranged in the table and renumbered in order of speed, beginning with the fastest, so as to make the dependence of the results upon the speed more clearly manifest. The first five experiments made early in December, 1907, were all consecutive; but that numbered 6 was executed long after the others (in January, 1908), after the vacuum jacket had been used for higher-boiling liquids, and had unfortunately cracked. Except for its somewhat larger warming correction, no essential difference could be detected between its results and that of the preceding experiment, carried out at the same rate. The last experiment was conducted under a pressure of 757 millimeters of mercury, the others were at normal pressure of 760 millimeters.

The table explains itself.

HEAT OF EVAPORATION OF WATER.

Series I, with Vaporizer I.

No. of experiment.	Observed weight condensed water (in air).	Time in minutes.	Time for one gram.	Rise of temperature corrected for radiation from vaporizer	Water equivalent total.	Difference between temperature of vaporization and mean temperature.	Heat of vaporization + heat of cooling to temperature of calorimeter.	Heat of vaporization of 1 gram (uncorrected) in 21° calories.
1	8.319	3.0	0.36	3.921	1307.6	78.9	616.3	537.4
2	10.514	5.0	0.48	4.927	1311.6	78.6	614.6	536.0
3	8.283	4.25	0.51	3.895	1307.8	78.8	614.9	536.1
4	9.558	8.5	0.89	4.473	1309.3	78.6	612.6	534.0
5	8.368	9.0	1.07	3.896	1310.2	78.3	609.9	531.6
6	8.398	9.0	1.07	3.916	1309.4	78.4	610.5	532.1

It will be noticed that the figure in the last column falls from 537.4 calories per gram, the result of the fastest determination, to 531.8 calories, in the two slowest—a change of about 1 per cent.

This definit march of the results seems to be referable only to the loss of heat by premature condensation in the part of the tube between the trap and the condenser—a defect in the method which is inevitable, for the vaporizer could hardly be brought closer to the calorimeter than it was in these experiments.

When the results are plotted, the values for the heat of vaporization being laid out in the direction of ordinates, and the time required for vaporization of 1 gram laid out in the direction of abscissas, the linear tendency of the results is manifest. The greatest departure of any single result from the straight line representing their average tendency is only 0.6 calorie, or 0.1 per cent. of the total thermal quantity being measured. This corresponds to an error of thermometric reading of 0.004°. The agreement therefore is as close as could be expected.

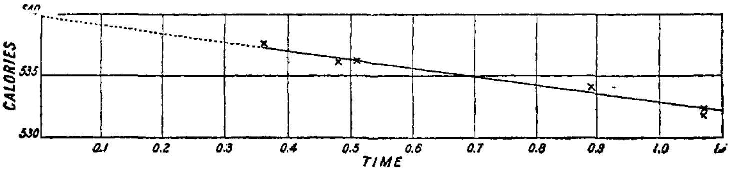

Fig. 6.—The heat of evaporation of water; first series. Time in fractions of a minute is plotted in the direction of abscissas, and heat of evaporation (in 21° calories) in the direction of ordinates. The dotted line is an extrapolation, giving the value for a hypothetical instantaneous experiment.

By extrapolation to zero time the value 539.6 (cal. 21°) is obtained for the heat of vaporization of a gram of water weighed in air—a value from which the effect of premature condensation must have been eliminated, because there is every reason to believe that this disturbing phenomenon is directly dependent upon the time consumed in the experiment, and that if the experiment could be performed instantaneously the error would wholly disappear. This value becomes 538.8 in terms of the calorie at 15°.

Inspection of the curve shows that the loss of heat in 1 minute must have been 7.0 small calories from this apparatus under these circumstances, and each of the results is evidently to be reduced to a common basis by adding to it this value multiplied by the fraction of a minute required for the vaporization of 1 gram. The results, then, become respectively 539.9, 539.4, 539.7, 540.2, 539.1 and 539.6, in the mean 539.6 (cal. 21°), essentially the same as the value found by the graphic extrapolation, upon which indeed the values are directly dependent.

Feeling that it was desirable to test these conclusions in another apparatus, a new vaporizer was made—unfortunately, however, with a somewhat wider and heavier exit tube. In this apparatus both the warming effect of the vaporizer upon the calorimeter and the loss of heat from premature condensation were greater than before—the former instead of being about 0.009° per minute became about 0.013, and the correction for premature condensation also increasing from 7 calories per minute to nearly 9.7 calories per minute. The determinations were also somewhat less concordant than before, as was to have been expected on account of the larger correction for radiation and conduction. Nevertheless they add valuable confirmatory evidence to the results given in the previous series, and accordingly are recorded in the following table arranged in the same way as those. Experiments 7, 8, 9, 10 and 11 were consecutive; and were made on the 7th and 8th of April, 1908. Experiment 12 was made at another time, but accords satisfactorily with 11, having about the same rate. During Nos. 7, 9 and 10 the barom-

HEAT OF EVAPORATION OF WATER.

Series II, with Vaporizer II.

No. of experiment.	Observed weight condensed water (in air).	Time in minutes.	Time for one gram.	Rise of temperature corrected for radiation from vaporizer.	Water equivalent total.	Difference between temperature of vaporization and mean temperature.	Heat of vaporization + heat of cooling to temperature of calorimeter.	Heat of vaporization of 1 gram (uncorrected) in 21° calories.
7	7.435	3.0	0.40	3.484	1309.0	78.62	613.5	534.9
8	7.170	3.0	0.42	3.376	1306.9	78.95	615.4	536.4
9	8.740	4.5	0.52	4.091	1308.6	78.54	612.5	534.0
10	8.625	5.0	0.58	4.034	1308.6	78.59	612.1	533.5
11	9.040	10.0	1.11	4.190	1310.1	78.69	607.3	528.6
12	9.150	10.0	1.09	4.250	1307.8	78.54	607.5	529.0

eter stood at 763 millimeters, during Nos. 8 and 11 at 766 millimeters, and during No. 12 at 762 millimeters.

On extrapolating the steeper but fairly consistent straight line drawn through these determinations, the value 539.3 (cal. 21°) is obtained for the heat of vaporization of a gram of water, a value only about 0.06 per cent. lower than that found in the previous series. A part of this difference is due to the slightly higher temperature of boiling in the second series, caused by the greater pressure.

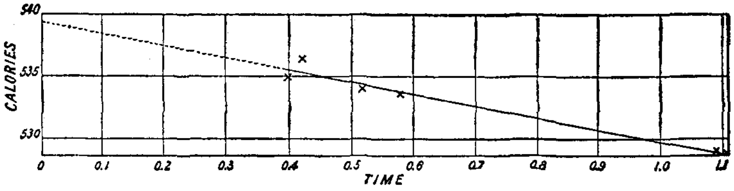

Fig. 7.—The heat of evaporation of water; second series. Time in fractions of a minute is plotted in the direction of abscissas, and heat of evaporation (in 21° calories) in the direction of ordinates. The dotted line is an extrapolation, giving the value for a hypothetical instantaneous experiment.

The individual determinations may be corrected by adding to them 9.65 multiplied by the time needed for vaporization of 1 gram, because the loss of heat is found through extrapolation to have been 9.65 small calories per minute. Corrected in this way the five determinations become respectively 538.8, 540.5, 539.0, 539.1, 539.3, on the average 539.3 as given before. The average of the results given in this series and those given in the previous series is 539.45. As the second decimal place has no significance, this may be rounded off to 539.5, giving the first series preference, partly because the pressure was more nearly normal, and partly because the apparatus was undoubtedly better and the series more concordant. This value becomes 538.7 in terms of the calorie at 15°. If the weight of the water is reduced to the vacuum standard, both of these figures are diminished by 0.11 per cent. The resulting values may be given in a brief table, together with the same quantity expressed in terms of the c. g. s. units:

FINAL RESULT.

Latent heat of evaporation at 100° of 1.0000 gram (in vacuum) of water equals:

538.9 cal.$_{21^\circ}$ or 0.5389 cal.$_{21^\circ}$
538.1 cal.$_{15^\circ}$ or 0.5381 cal.$_{15^\circ}$
2251 joules or 2.251 kilojoules

In all the subsequent work the first vaporizer was used, even although its vacuum had been destroyed; and it continued to give excellent results with other substances. The communication of these results must be left for a future publication, partly because the necessary specific heats of the liquids are not yet well enough known. One point, however, in connection with the results may advantageously be mentioned here, because it strengthens highly one's faith in the method of extrapolation employed to eliminate the effect of premature condensation. The loss of heat per gram was 7 calories per minute with steam in the best apparatus (Vaporizer I). With liquids of lower boiling point the loss should be less; with liquids of higher boiling point the loss should be more, if the inference is really justified. As a matter of fact precisely this phenomenon was noticed with different liquids. For example in the case of benzene, where the difference between the temperature of the vaporizer and that of the calorimeter amounted to 60° instead of to about 80°, the loss per minute amounted to about 5.2 calories per minute [1] a figure strictly proportional to the number 7.0 found in the case of water. Again with ethyl butyrate, boiling at 122°, the difference between the temperature of the vaporizer and that of the calorimeter was 102° instead of 80°, a fall of temperature which should correspond to a loss of heat of about 9 calories per minute, and the actual loss was found to be about 9.2 calories per minute, an amount as close as could be expected to the computed result. Moreover, in the case of methyl formate, boiling at 32°, the time of the experiment made practically no difference at all in the observed value for the heat of vaporization. Thus t seems perfectly clear that the march in the results is really due to an illicit loss of heat, and that the method employed for correcting the results is the best that can be devized. In conclusion the remark may be made that unfortunate as this inevitable difficulty with the method is, it is no more unfortunate than similar difficulties which come into any other method for determining the latent heat of vaporization. As has been more than once pointed out, the very nature of the problem renders impossible a method wholly free from some sort of correction. Even Henning's far more complicated method had its own difficulties of a somewhat similar kind, as a perusal of his paper will show.

The comparison of our value for the heat of vaporization of a gram of water weighed in vacuum, 538.9 cal._{21° (or 538.1 cal._{15°), with the work of others, speaks strongly in its favor. The value given by Regnault, 536.7, is unquestionably too low. Henning's value 538.25 cal._{15° was found at 100.6°. Corrected to 100°, this would be 538.7 cal._{15°, a value only a trifle above ours. Joly,[2] Harker[3] and Smith,[3] likewise obtained values near 540.

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[1] This figure applies only to Vaporizer I, not to the preliminary form used in the benzene series given on p. 13. In the early form the loss per minute was over 9 calories with benzene.

[2] *Phil. Trans.*, **186**, 322 (1895). Dependent on Joly's value for the mean calorie between 12° and 100°.

[3] *Loc. cit.*

In conclusion we are glad to express our gratitude to the Carnegie Institution of Washington, for generous pecuniary assistance.

Summary.

1. The method of Berthelot and Kahlenberg for determining heats of vaporization has been modified in such a way as to diminish greatly the errors inherent in the experimentation. A Dewar vessel was used as a vaporizer and the calorimetric work was strictly adiabatic.

2. A serious persistent disturbing effect, amounting to about 0.1 per cent. of the total per minute, was eliminated by conducting experiments at different speeds and extrapolating the results to a hypothetical instantaneous experiment from which the disturbing effect may be supposed to be eliminated, because this was found to depend essentially upon time. The disturbing effect was probably premature condensation in the very narrow zone between the vaporizer and the condenser.

3. The heat of vaporization of a true gram of water was found by this method to be 538.9 $\text{cal.}_{21}{}^{\circ}$ or 2.251 kilojoules per gram. A gram molecule therefore requires 9.707 $\text{cal.}_{21}{}^{\circ}$ or 40.54 kilojoules, when the vaporization is conducted at 100° ($O = 16.000$, $1\ \text{cal.}_{21}{}^{\circ} = 4.177$ kilojoules).

4. Comparison of this figure with the results of others shows that the method is trustworthy and suitable for general use.

5. Numerous other liquids also have been used in the apparatus, and consistent results with them have been obtained. These will be communicated in a future paper, when the specific heats of the liquids have been determined.

CAMBRIDGE, MASS.

THE POSSIBLE SOLID SOLUTION OF WATER IN CRYSTALS.

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In a recent paper Perdue and Hulett[1] have published the results of several careful analyses of cadmium sulfate, which deserve an adequate explanation. According to these determinations the amount of cadmium both in the hydrated sulfate and in the anhydrous sulfate is less than that required by the usually accepted atomic weight of cadmium, sulfur, oxygen and hydrogen, and the formulas $3CdSO_4.8H_2O$ and $CdSO_4$ respectively.

The determination of the cadmium seems to have been well executed; the experimenters adopted two well known and long tested methods, namely, the use of mercury as a receptacle for the electrolytic precipitate

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[1] Perdue and Hulett, *J. Physic. Chem.*, 15, 147 (1911).