A REVIEW OF CALORIMETRIC MEASUREMENTS ON THERMAL PROPERTIES OF SATURATED WATER AND STEAM

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ABSTRACT

This review has been prepared to assemble the data which are now available on the calorimetric determinations of the thermal properties of saturated water and steam and to reduce them to a uniform basis for comparison. After a careful analysis of the reports which have appeared in the literature an attempt is made to point out some possible causes for the variation among the recorded results. Wherever it seemed desirable, a thermodynamic interpretation of the experiments is given, and in a number of cases the data have been recalculated. By these means the agreement among the various determinations has been improved in several instances.

It is hoped that this assembly of results presented on a uniform basis may serve as an aid to future International Steam Table Conferences in the choice of base values and tolerances for the International Skeleton Tables.

By means of deviation charts the experimental values for the heat content or enthalpy of the saturated liquid and for the latent heat are exhibited and compared. The agreement is, in general, quite gratifying.

Several modern steam tables are compared graphically with one another and with the National Bureau of Standards experimental results on the thermal properties of the saturated liquid and vapor. A marked improvement in the tables is evident with the increase in scope and the reliability of the basic experimental data.

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I. INTRODUCTION

There have been numerous attempts in the past to formulate the thermal properties of water and steam, by means of equations, into tables convenient for the use of engineers. These formulations have,

through necessity, been based on scattered groups of experimental data, recorded by different investigators in a great variety of units. For the most part the variations in the tabulated values in steam tables may be attributed to three causes. First, the choice of various forms of empirical relations to fit data which in themselves are scattered and somewhat discordant; second, the confusion arising from the use of the different measuring standards; third, the thermodynamic interpretation of the experimental data.

An important advance in the evolution of steam tables was made by the International Steam Table Conference at London in July, 1929. One accomplishment of this conference [1] [2] [3] was the establishment of an International Skeleton Table, with tolerances, of the thermal properties of water and steam. It was anticipated that the table there adopted was subject to revision by subsequent conferences with the idea of narrowing the limits and approaching more closely the true values.

The publication of the data from the calorimetric determinations at the Bureau of Standards, presenting new values for the thermal properties of steam over a large portion of the saturation region, has suggested the need of a summary of all available data of a similar kind. This review is given as a supplement, appearing simultaneously with the detailed report of the Bureau of Standards determinations [4] to aid in the comparison of these results with those previously published. By the reduction of all the data to a uniform basis for comparison it is hoped that the review may serve as an aid in the choice of basic values and tolerances for the International Skeleton Steam Table.

It is often possible, by studying the published descriptions, to reveal important evidence as to reliability, and it has been the aim in this review to bring out such evidence. It is gratifying to find that, in some cases, careful analysis and reduction of published data are rewarded by improvement in the agreement of the results.

The experiments in this field fall logically into two groups: (1) Determinations of the heat content or enthalpy of the liquid, and (2) determinations of the heat of vaporization. The various experiments of each group will be discussed in chronological order as far as is practicable.

II. NOTATION

M = mass of fluid.
m = mass of saturated vapor.
θ = temperature, centigrade.
Θ = temperature, centigrade absolute.
π = saturation vapor pressure.
P = external pressure.
V = internal volume of container for water.
u = specific volume of saturated liquid.
u' = specific volume of saturated vapor.
x = fraction of the water which is vapor.
E_x = internal energy of entire water sample.
ϵ = internal energy per gram of saturated liquid.

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[1] Eng., 128, pp. 751–752; 1929.
[2] Zeit. des V. D. I., 73, No. 52, pp. 1856–1858; 1929.
[3] Mech. Eng., 52, pp. 120–122; 1930.
[4] B. S. Jour. Research, 5 (RP209), pp. 411–480; 1930.

ϵ' = internal energy per gram of saturated vapor.
H = heat content per gram of saturated liquid $(\epsilon + \pi u)$.
H' = heat content per gram of saturated vapor $(\epsilon' + \pi u')$.
L = heat of vaporization per gram $= H' - H$.

$$\alpha = H - L\frac{u}{u'-u} = H - \beta$$

$$\beta = \frac{Lu}{u'-u}$$

$$\gamma = L + L\frac{u}{u'-u} = L\frac{u'}{u'-u}$$

$$L = \theta\frac{d\pi}{d\theta}(u'-u) \quad \text{(Clapeyron equation)}$$

III. ANALYSIS AND REDUCTION OF SOURCE DATA

1. DETERMINATIONS OF HEAT CONTENT OF THE LIQUID

In the temperature range from 0° to 100° C. the investigations have been numerous and particularly painstaking, because the calorie was used as a primary unit of energy and much effort was expended in determining the precise relation between this and other units of energy. This latter knowledge has been necessary in order that all calorimetric data could be reduced to a common basis for comparison. If, as has already been attempted, a heat unit defined arbitrarily and directly in terms of mechanical units is universally adopted and used, the need for these so-called mechanical equivalents of heat vanishes as far as future work is concerned. The difficulties encountered in the preparation of this review emphasize the advantages of adopting some such arbitrarily defined heat unit.

That the experimental determination of the mechanical equivalent of heat referred to water is a difficult task is evidenced in the literature by the diversity of the results recorded. Even after the most careful attempts to reduce the experimental values to a uniform basis, there still exist divergent values for the mechanical equivalents of the various calories.

Since many of the past determinations of heat capacities and of ratios of these give little important information about the heat content, they are accorded only passing mention in this review. More important among them are determinations by Rowland,[5] Griffiths,[6] Schuster and Gannon,[7] Lüdin,[8] Callendar,[9] Romberg,[10] and Laby and Hercus.[11] The results of Barnes,[12] and of Jaeger and von Steinwehr [13] yield, on integration, values of heat content which will be discussed more fully later.

(a) REGNAULT

For a long time the classical work of Regnault [14] furnished the most reliable information available on the specific and latent heats of water.

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[5] Proc. Am. Acad. of Arts & Sci., **15**, pp. 75–200; 1879.
[6] Phil. Trans. Roy. Soc. London, **A184**, pp. 361–504; 1893.
[7] Phil. Trans. Roy. Soc. London, **A186**, Pt. I, pp. 415–467; 1895.
[8] Die Abhängigkeit der specifischen Warme des Wassers von der Temperatur. Inaug. Diss., Zürich; 1895.
[9] Phil. Trans. Roy. Soc. London, **A199**, pp. 55–148; 1902.
[10] Proc. Am. Acad. of Arts & Sci., **57**, pp. 377–387; 1921–22.
[11] Phil. Trans. Roy. Soc. London, **A227**, pp. 63–92; 1927.
[12] Phil. Trans. Roy. Soc. London, **A199**, pp. 149–263; 1902.
[13] Ann. Phys., **369**, pp. 305–366; 1921.
[14] Relations des Expériences, **1**, 635–748; 1847.

At the time these researches were carried out the physical sciences were in their infancy, but in spite of the many difficulties Regnault's conclusions were remarkably accurate. In the 50 years that followed no similar experiments on water and steam comparable in accuracy are recorded.

No matter how carefully his experiments were done, they could not have yielded results as near to the truth as can now be obtained with the aid of more advanced theory, more definitely established standards, and improved laboratory apparatus. It is not possible, with any considerable degree of certainty, to interpret the temperatures which he recorded, in terms of the present international scale. For these reasons, no attempt will here be made to reduce his results to a comparative basis. They are considered instead as an important milestone which it took years to reach, but which has now been left far behind.

(b) REYNOLDS AND MOORBY

In the experiments of Reynolds and Moorby [15] the value of the mean calorie was measured directly in terms of mechanical units with a modified Froude brake. This work was done on an engineering scale, and many precautions were taken to insure the precision of the results. The principal corrections were for thermal leakage and liberation of dissolved air. Some errors were probably introduced by formation of vapor, by variations in the speed at which the driving engine ran, and because thermometry at that time was not on an entirely satisfactory basis. On the average the water entered the brake at a temperature of about 1.3° C. and a pressure of about 2 atmospheres and left it at a temperature of about 100° C. and a pressure of about 1.8 atmospheres. A correction was applied for the energy change due to the pressure drop through the system, so that the value recorded is the mean specific heat of water between 1.3° and 100° C. at a constant pressure of 2 atmospheres. As the mean of 26 separate determinations Reynolds and Moorby report this mechanical equivalent as 4.1832×10^7 ergs per gram ° C. along the 2 atmosphere line. If the figure 1.0004 [16] is taken as the ratio between the international and the absolute joule, this value becomes 4.1815 international joules per gram ° C. It may be further corrected to the saturation path by the following method.

The value for the change in heat content with pressure at constant temperature can be evaluated through the relation

$$\left(\frac{\partial H}{\partial P}\right)_\theta = V - \theta\left(\frac{\partial V}{\partial \theta}\right)_p \tag{1}$$

in which the right-hand member can be evaluated with sufficient precision from data on specific volumes and coefficients of thermal expansion given in the International Critical Tables. The corrections desired are then the products $\left(\frac{\partial H}{\partial P}\right)_\theta (1-\pi)$ when the values $\pi = 0.0066$ atmospheres at 1.3° and $\pi = 1$ atmosphere at 100° are substituted. The change in heat content along the saturation path from 1.3° to 100° is greater by $0.206 - 0.076 = 0.13$ international joules per gram than it is along the 2 atmosphere path.

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[15] Phil. Trans. Roy. Soc. London, **A 190**, pp. 301–422; 1897.
[16] Bureau of Standards Tech. News Bul.; April, 1930.

Reynolds and Moorby's value for the change in heat content from 1.3° to 100° along the saturation path becomes $4.1815 \times 98.7 + 0.13 = 412.84$ international joules per gram. The value for the change in heat content of water between 0° and 100° is obtained by adding to this the Bureau of Standards value for the change in H from 0° to 1.3° = 5.49 international joules per gram. The result thus obtained from the work of Reynolds and Moorby is 418.33 international joules per gram for the change in heat content of water between 0° and 100° along the saturation path.

(c) DIETERICI

Dieterici's [17] experiments consisted in the introduction of quartz tubes at known temperatures, first empty and then containing known masses of water, into a Bunsen ice calorimeter and observing the contraction in volume due to the fusion of ice. This contraction, which he expressed in milligrams of mercury, is a measure of the heat lost by the tube or the tube and contents when its temperature changed from the initial value θ, to 0° C. By difference the contraction due to the cooling of the water sample alone was obtained. Expressing by $Q\Big]_0^\theta$ this heat lost by the water and by C_m an integrated mean specific heat which is to be experimentally determined, Dieterici's results were evaluated through the equation

$$Q\Big]_0^\theta = m\rho\Big]_0^\theta + \Big[MC_m\theta\Big]_0^\theta \tag{2}$$

in which

$$m\rho\Big]_0^\theta = \left[(V-Mu)\left(\Theta\frac{d\pi}{d\theta}-\pi\right)\right]_0^\theta \tag{3}$$

This correction $m\rho\Big]_0^\theta$ takes into account the energy changes in the ever-present vapor phase. Since the volume change of the retaining tubes due to changes in temperature and pressure is negligible, the heat exchange of the contents becomes identical with the loss of internal energy.

For any state

$$E_x = Mx\epsilon' + M(1-x)\epsilon = M\epsilon + Mx(\epsilon'-\epsilon) \tag{4}$$

and

$$V = Mxu' + M(1-x)u = Mu + Mx(u'-u) \tag{5}$$

Solving

$$x = \frac{V-Mu}{M(u'-u)} \tag{6}$$

Hence

$$E_x = M\epsilon + (V-Mu)\frac{\epsilon'-\epsilon}{u'-u} \tag{7}$$

But

$$L = \epsilon' - \epsilon + \pi(u'-u) = \Theta\frac{d\pi}{d\theta}(u'-u) \tag{8}$$

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[17] Dieterici, Ann. Phys., **321**, pp. 593–620; 1905.

Hence

$$\frac{\epsilon'-\epsilon}{u'-u}=\Theta\frac{d\pi}{d\theta}-\pi \tag{9}$$

and

$$E_x=M\epsilon+(V-Mu)\left(\Theta\frac{d\pi}{d\theta}-\pi\right) \tag{10}$$

But

$$Q\Big]_0^\theta=E_x\Big]_0^\theta=\left[MC_m\theta\right]_0^\theta+\left[(V-Mu)\left(\Theta\frac{d\pi}{d\theta}-\pi\right)\right]_0^\theta \tag{11}$$

From which

$$\left[C_m\theta\right]_0^\theta=\epsilon\Big]_0^\theta \tag{12}$$

Dieterici records experimental values of C_m and θ, and, as shown, the product of these is the specific internal-energy change of the saturated liquid. His values of the correction term $m\rho\Big]_0^\theta=\left[(V-Mu)\left(\Theta\frac{d\pi}{d\theta}-\pi\right)\right]_0^\theta$ were calculated from the best values of u, π, and $\frac{d\pi}{d\theta}$ then available. In order that the values of the contractions which he observed in milligrams of mercury could be converted into more convenient units he made very careful direct determinations of the volume changes produced by the addition of measured quantities of electrical energy.

With the experimental data now available it is possible to interpret his results directly in international joules without reference to his experimentally determined electrical equivalent of the calorimetrically observed quantity. His results at 100° C. furnish in effect a direct determination of the equivalent of the mean calorie in terms of milligrams of mercury. This value in milligrams of mercury corresponds to the value of the mean calorie in international joules, which is now known to a greater precision than he could have obtained with his observations on electrical equivalent. When this method is used to calculate the results of his measurements all difficulties arising from the evaluation of his electrical standards and from the changes which electrical units have since undergone are avoided.

From recent experiments it is possible to evaluate the correction term $m\rho]_o^\theta$ more exactly than before. At the same time a term of the magnitude πu can be introduced to convert the internal energy changes into changes of heat content.

As above

$$Q]_o^\theta=M\epsilon]_o^\theta+\left[(V-Mu)\left(\Theta\frac{d\pi}{d\theta}-\pi\right)\right]_0^\theta \tag{13}$$

But

$$\Theta\frac{d\pi}{d\theta}=\frac{L}{u'-u}=\frac{\beta}{u} \tag{14}$$

Hence

$$Q]_o^\theta=M\epsilon]_o^\theta+\left[(V-Mu)\left(\frac{\beta}{u}-\pi\right)\right]_0^\theta \tag{15}$$

Adding $M\pi u]_o^\theta$ to both sides

$$Q]_o^\theta + M\pi u]_o^\theta = M\epsilon]_o^\theta + M\pi u]_o^\theta + \left[(V - Mu)\left(\frac{\beta}{u} - \pi\right)\right]_o^\theta \tag{16}$$

Whence

$$Q]_o^\theta + M\pi u]_o^\theta = MH]_o^\theta + \left[(V - Mu)\left(\frac{\beta}{u} - \pi\right)\right]_o^\theta \tag{17}$$

Expanding and collecting

$$Q]_o^\theta = MH]_o^\theta + \left[V\left(\frac{\beta}{u} - \pi\right)\right]_o^\theta - M\beta\Big]_o^\theta \tag{18}$$

But

$$H]_o^\theta = [\alpha + \beta]_o^\theta \tag{19}$$

Hence

$$Q]_o^\theta = M\alpha]_o^\theta + \left[V\left(\frac{\beta}{u} - \pi\right)\right]_o^\theta \tag{20}$$

Considering now the experiments at 100° C., if $Q]_0^\theta$ is expressed in milligrams of mercury and both terms in the right-hand member in international joules, we may write

$$KQ]_o^\theta = M\alpha]_o^\theta + \left[V\left(\frac{\beta}{u} - \pi\right)\right]_o^\theta \tag{21}$$

from which the value of the conversion factor K can be determined. Values of α and β are obtainable from the previous paper,[18] and values of π and u, which enter only in the relatively small correction term, from the best sources now available. There are 13 experiments in the neighborhood of 100° each of which yields a value of K.

The 13 values of K thus obtained yield a mean value of 0.27024 international joules per milligram of mercury, when the experiments are weighted according to Dieterici's estimate of their reliability. They are very consistent, the maximum deviation from the mean being about 1 in 720 and the average 1 in 1,380. The accuracy of the chosen mean value of K is doubtless greater than the experimental accuracy at temperatures other than 100°, because of the greater number of experiments performed at that temperature, and because of the comparative ease of maintaining and determining the steam point.

To transform equation (20) given above into a form convenient for the calculation of heat content, add $M\beta]_0^\theta$ to both sides and collect.

$$M\alpha]_o^\theta + M\beta]_o^\theta = 0.27024\ Q]_o^\theta - \left[V\left(\frac{\beta}{u} - \pi\right)\right]_o^\theta + M\beta]_o^\theta = MH]_o^\theta \tag{22}$$

$$H]_o^\theta = \frac{0.27024\ Q]_o^\theta}{M} - \frac{V}{M}\left[\frac{\beta}{u} - \pi\right]_o^\theta + \beta]_o^\theta \tag{23}$$

At any temperature the terms in the right-hand member of this equation can be evaluated from the same sources as at 100°. Dieterici's data give the values of $Q]_o^\theta$ corrected for heat leak, the values of M corrected for buoyancy, and the measured values of V. Hence, $H]_o^\theta$ can be evaluated at each temperature for which data are given.

[18] See footnote 4, p. 482.

Making use of the Bureau of Standards data, his values of H have been reduced to even temperatures for convenience in making comparisons with others. Table 1 shows the results of Dieterici's experiments as obtained by this method of calculation.

TABLE 1.—*Heat content of saturated liquid water calculated from Dieterici's experiments*

Temperature, θ °C.	Heat content, H	Temperature, θ °C.	Heat content, H
	Int. joules per g		*Int. joules per g*
15	63.10	100	[1] 418.75
20	83.82	110	461.1
25	104.6	130	546.6
30	125.6	156	660.6
35	146.2	183	776.5
46	192.2	200	852.6
56	234.2	221	946.2
65	271.8	240	1,034.7
78	326.4	259	1,126.7
88	368.2	303	1,348.9

[1] This value has been made to correspond exactly with the Bureau of Standards value by the method of computation.

The accuracy of the temperature measurements, which were made with mercury in glass thermometers, calibrated at the Reichsanstalt, was probably so good that the thermometry did not limit the over-all accuracy of the experiments. How nearly the water containers assumed the same temperature as that observed for the bath is less certain. Heat-leak corrections were small, and though there is little discussion of how they were obtained, it is believed that they furnished only a minor portion of the error in the final results. At the high temperatures the values of V become more significant, and higher precision in the determination of these would have increased the accuracy of the results. As a whole the research seems to have been carried out with great care and skill and claims the admiration of the careful reader.

(d) BARNES

Barnes [19] gives a very detailed account of his researches on the heat capacity of water between 5° and 95°, using a flow calorimeter of the so-called "continuous electric" type designed in cooperation with Callendar.[20]

Water was admitted into a vacuum-jacketed glass calorimeter at a steady but controllable rate, and its temperature was raised by means of an electric heater located in the stream between a pair of differential resistance thermometers which indicated the temperature rise. The amount of water which had passed through the calorimeter was determined by weighing. The experiments were performed at a constant pressure differing from the atmospheric pressure by the small pressure head used to maintain the flow.

For the electrical equivalent of the mean specific heat between 5° and 95° Barnes gives 4.1888 joules, referred to the international ohm and the volt defined as 1/1.4342 of the emf of the Clark cell at 15°.

[19] See footnote 12, p. 483.

[20] See footnote 9, p. 483.

In a recomputation of his results in 1909 [21] he expressed the belief that the voltage of the Clark cells at 15° as used in 1902 was 1.4333. This reduces the results previously published by 1 part in 798. Thus recomputed, the value of 4.1888 joules per gram for the mean specific heat between 5° and 95° becomes 4.1835 joules per gram. Correcting for the end intervals he obtained the value 4.1849 international joules per gram for the equivalent of the mean calorie along the atmospheric-pressure path. In 1910 the value of the international volt was reassigned, using as a standard the Weston normal cell having an emf at 20° of 1.0183 international volts. In terms of this standard of 1910, Clark cells, made up according to the old specification, have an emf at 15° of 1.4328 volts.[22] This may be considered at least a probable value for the Clark cells used by Barnes in terms of the present system. This value further reduces his mechanical equivalent of the mean calorie along the atmospheric-pressure path by 1 part in 1,433, to 4.1820 international joules per gram. This value, corrected to saturation pressure, becomes 4.1830 international joules per gram.

In Laby's [23] critical discussion of the mechanical equivalent of heat, the results of Barnes, among others, are reduced to absolute units. Since the values are desired here in international units, and since Laby discusses only the 20° calorie, no comparison with the results given in his review is included.

Without reference to the report of Barnes in 1909, his values for the specific heats can be transformed into present international units as follows. In his original computations the value assigned to the Clark cell at 15° was 1.4342 volts. As stated above, the emf of Clark cells made up according to the same specifications is 1.4328 international volts. Therefore, the values of specific heat as originally reported can be transformed into present international joules by reducing them by 1 part in 512.

Barnes represents his data as finally reduced by three equations, appropriate over the temperature intervals indicated.

$$(5°\text{–}37.5°) \quad C_p = 0.99722 + 0.0000035\,(37.5-\theta)^2 + 0.00000010\,(37.5-\theta)^3 \tag{24}$$

$$(37.5°\text{–}55°) \quad C_p = 0.99722 + 0.0000035\,(\theta-37.5)^2 + 0.00000010(\theta-37.5)^3 \tag{25}$$

$$(50°\text{–}100°) \quad C_p = 0.99839 + 0.000120(\theta-55) + 0.00000025(\theta-55)^2 \tag{26}$$

These are in terms of his own mean calorie, and yield on integration with respect to temperature, values for the changes in heat content in mean calories. The integrated equations are

$$H]_5^\theta = 0.99722 - 0.00000117\,(37.5-\theta)^3 - 0.000000025\,(37.5-\theta)^4 \tag{27}$$

$$H]_{37.5}^\theta = 0.99722 + 0.00000117\,(\theta-37.5)^3 + 0.000000025\,(\theta-37.5)^4 \tag{28}$$

$$H]_{55}^\theta = 0.99839 + 0.000060\,(\theta-55)^2 + 0.000000083\,(\theta-55)^3 \tag{29}$$

To transform the values calculated from these equations into a form convenient for comparison, two further corrections are applied.

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[21] Proc. Roy. Soc. London, **82**, pp. 390–395; 1909.
[22] B. S. Circular No. 60, p. 41; 1920.
[23] Proc. Phys. Soc. London, **38**, pp. 169–175; 1925–26.

Since the first equation is valid only down to 5°, the value of $H^5_0 = 5.02$ mean calories is supplied from the Bureau of Standards data. Further correction is necessary to reduce the results to the saturation pressure for each temperature recorded. The method of calculation of these corrections has already been described. Table 2 gives the values of heat content calculated from Barnes's equations, the corrections to reduce them to the saturation pressures and in the last column the values along the saturation path. The figure 418.30 international joules per gram as derived above from Barnes's own measurements is used for the conversion of mean calories to international joules.

TABLE 2.—*Heat content from Barnes's specific heat equations*

Temperature θ	Heat content $P=1$ atmosphere, $H_{1\ atm.}$	$\left(\frac{dH}{dP}\right)_\theta \times (1-\pi)$	Heat content H, $P=\pi$	Heat content H, $P=\pi$
° C.	*Mean calories/g*	*Mean calories/g*	*Mean calories/g*	*Int. joules/g*
10	10.03	0.02	10.05	42.04
20	20.04	.02	20.06	83.91
30	30.02	.02	30.04	125.66
40	39.99	.02	40.01	167.36
50	49.97	.02	49.99	209.11
60	59.95	.02	59.97	250.85
70	69.95	.01	69.96	292.64
80	79.96	.01	79.97	334.51
90	89.98	.00	89.98	376.39
100	100.01	.00	100.01	418.30

The chief uncertainty in the value of the heat content of water at 100° expressed in international joules per gram from the experiments of Barnes lies in the interpretation of the emf of the Clark cells used. The value which seems most probable to the reviewer is 418.30 international joules per gram.

In a glass apparatus of the type used by Barnes the evaluation of the heat leak (4 per cent of the total energy supplied in the extreme case), including the heat effects observed and interpreted as due to adsorption or liberation of residual gas in the evacuated jacket, is a difficult task.

The temperature scale used in these experiments was substantially the same as the present international scale. Observations of temperature differences with the differential resistance thermometers were probably sufficiently precise. The precision with which the electrical measurements were made appears to have been ample. The assumption that the walls of the weighing vessel always retained the same mass of liquid may have been a source of error. The possibility of formation of vapor and liberation of dissolved gas within the calorimeter are inherent in the method and the effects are difficult to evaluate.

To obtain an accuracy of better than 1 part in 1,000 in this type of experiment requires a degree of refinement in the calorimetry itself which is not easily attained. It appears that there may have been possible sources of systematic error, some of which have been mentioned and several of which may have exceeded 1 part in 10,000. In the absence of positive supporting evidence it seems that Barnes's estimate of accuracy of 1 part in 10,000 may have been too optimistic.

The reader of Barnes's report is impressed with the remarkable care and skill with which the experimental program was planned and

executed, and this piece of work remains one of the outstanding contributions to our knowledge of the heat capacity of water.

(e) CALLENDAR

Callendar spent many years in the investigation and formulation of the properties of steam. In his work on the liquid he is responsible for the development of two types of calorimetry which he has described as the continuous electric method and the continuous mixture method. The former method was used by Barnes in the researches already described and the results of this investigation are correctly attributed to Callendar and Barnes. At a later date Callendar [24] alone performed experiments by the second method to test the ratios of the specific heats reported by Barnes and found good agreement between the methods. He stated that the method of mixtures was more dependable than the electric method because the heat leak was reduced from about 4 per cent to about ½ per cent of the total energy changes involved.

In not only this work of 1912 but also in all the succeeding reports which Callendar has published the reviewer has little opportunity to appraise the experimental work, as such, because practically no experimental data are given. Instead, Callendar has chosen always to formulate his experimental data through equations into tables of the properties most desired. These tables must be taken as representing the best values indicated by his own experiments, but the data of other observers are included in the reductions in such a way that it is impossible to separate them.

Beyond the knowledge that Callendar was an exceptionally brilliant, skillful, and painstaking experimenter who devoted much time to investigations in his chosen field, the lack of published experimental data precludes an estimation of the absolute accuracy of his experimental results, or the agreement between these results and his tabulated values.

Therefore, for the purposes of this comparison, the values taken from his latest steam tables [25] are used as best representative of his entire group of measurements.

Callendar's equation for the heat content of the liquid is

$$H=k(\theta-c)+\frac{Lu}{u'-u} \tag{30}$$

in which k and c are constants. The last term in this equation is the quantity β measured experimentally at the Bureau of Standards, and from the relation

$$H=\alpha+\beta \tag{31}$$

it follows directly that, according to the Callendar formula,

$$\alpha=k\ (\theta-c) \tag{32}$$

and that

$$\frac{d\alpha}{d\theta}=k \tag{33}$$

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[24] Phil. Trans. Roy. Soc. London, A212, pp. 1–32, 1912–13.
[25] Proc. Inst. Mech. Eng., No. 3, pp. 507–527; 1929.

The quantity α has been very carefully determined by direct calorimetric measurements at this bureau at each 10° interval from 0° to 270°. These results indicate that the value of $\frac{d\alpha}{d\theta}$ is practically constant in the range 50° to 170°, but outside this range it varies considerably. Callendar recognized that his equation was inadequate in the region from 0° to the temperature of the minimum specific heat of water, but accepted it nevertheless, because of its simplicity, its degree of approximation to the truth, and the relative unimportance to the engineers of the values calculated from it in the range near the freezing point. His own experimental evidence confirming the validity of the equations at high temperatures is not at hand. According to the Bureau of Standards data the value of $\frac{d\alpha}{d\theta}$ decreases from a practically constant value of 4.17 international joules per gram °C. in the range 50° to 170° to about 4.10 international joules per gram °C. at 270°.

Since the quantity $\beta=\frac{Lu}{u'-u}$ is small in comparison with α, the discrepancy in the values of H at the higher temperatures is due largely to the difference in the evaluation of the variation of α with temperature.

Callendar's values of H' doubtless have as a basis his numerous experiments in the superheat region. His values of H are from the equation discussed above, which was based on the work of Callendar, Barnes, and probably Dieterici in the high temperature range.

In Table 3 are shown, in international joules, the values of H and H' from the most recently published Extended Steam Tables.[26]

TABLE 3.—*Callendar's values of heat content*

Temperature θ	Heat content—	
	Of liquid H	Of vapor H'
°C.	*Int. joules/g*	*Int. joules/g*
0	0	2,488.3
50	208.77	2,584.2
100	418.54	2,675.7
150	631.62	2,751.8
200	852.14	2,801.7
250	1,087.36	2,818.4
270	1,187.81	2,811.3

(f) JAEGER AND VON STEINWEHR

The experiments of Jaeger and von Steinwehr on the heat capacity of water from 5° to 50° C., performed in 1911–12 and published in 1915 [27] and more completely in 1921,[28] have been the basis for the value of the 15° calorie used by the Reichsanstalt. Their calorimeter, containing 50 liters of water at atmospheric pressure, was heated electrically, in steps of about 1.4°, and the rise in temperature was observed with resistance thermometers. A stirrer aided in the

[26] See footnote 25, p. 491.
[27] Sitzungber d. Berl. Akad., p. 424; 1915.
[28] See footnote 13, p. 483.

distribution of the heat added, and itself added mechanical energy at the rate of over 60 joules per minute. The heat capacity of the calorimeter, stirrer, and accessories was calculated from the masses of the parts and their specific heats and was considered constant over the temperature range covered. The time of electrical heating was automatically recorded with sufficient precision by a chronograph. The temperature scale and the electrical units employed were substantially those now in use by international agreement.

The evaluation of the correction, which includes thermal leakage and pump energy, was carried to considerable lengths theoretically, but there is some doubt that the values so obtained were sufficiently accurate. No statement was made concerning the constancy of the pump speed.

In an effort to gain sensitivity the measuring current through the thermometer was increased to 0.08 ampere. Such a procedure throws doubt upon the accurate indication of temperature changes to 0.0001°, because of the heating of the thermometer itself. This suspicion is supported by the fact that a considerable rate of stirring was required in order that the temperature change of the calorimeter would appear regular during the periods when no energy was being supplied in the heating coil. The temperature intervals were so small that the assumption of the constancy of the specific heat in any interval was entirely justified.

The capacity of the calorimeter was chosen so that the mass of the water sample was large compared to the water equivalent. The calorimeter was not tightly sealed, and there was the possibility of the loss of water vapor. Great care was taken with the electrical measurements, and the only questionable point here is the heating of the standard 0.1 ohm resistor, due to the current in it, during observations of the current through the heater.

From a total of 111 experiments 37 were rejected because of known faults in manipulation, etc. An empirical equation of specific heat as a function of temperature was fitted to the remaining 74 points by the method of least squares. The consistency of the experimental points is indicated by the fact that they lie so well on a smooth curve, the average deviation from the curve being 1 part in 2,350.

Their equation

$$C_p = 4.20477 - 0.001768\theta + 0.000026447\theta^2 \qquad (34)$$

yields on integration with respect to temperature

$$\int_1^2 C_p d\theta = H]_1^2 = 4.20477\theta]_1^2 - 0.000884\theta^2]_1^2 + 0.000008816\theta^3]_1^2 \qquad (35)$$

The values of changes in heat content along the atmospheric-pressure path can be computed from this equation. Corrections to the saturation path are the same as those given in the discussion of the work of Barnes.

Table 4 shows in column 2 the values of H for water under a constant pressure of 1 atmosphere from the above equation, in column 3 the corrections necessary to reduce these to saturation pressures, and in column 4 the values thus reduced.

TABLE 4.—*Heat content from Jaeger and von Steinwehr's specific heat equation*

Temperature θ	Heat content $P=1$ atmosphere, $H_{1\ atm.}$	$\left(\frac{\partial H}{\partial P}\right)_\theta (1-\pi)$	Heat content H $P=\pi$,
° C.	*Int. joules/g*	*Int. joules/g*	*Int. joules/g*
10	41.97	0.10	42.07
20	83.82	.10	83.92
30	125.59	..09	125.68
40	167.34	.08	167.42
50	209.13	.08	209.21

2. DETERMINATIONS OF LATENT HEAT

(a) DIETERICI

Using a Bunsen ice calorimeter, Dieterici [29] made 20 determinations of the latent heat of water at 0° C. Considering the early date of this work and the comparative simplicity of his apparatus the results seem remarkably good. He vaporized the water at pressures slightly below the vapor pressure at 0° C. from small containers of glass or of platinum surrounded by a considerable quantity of mercury and observed the increase in volume of the ice-water mixture in the calorimeter around the mercury. Several errors could have affected the final results. Some water would have been lost as vapor from the capsule between the time it was weighed and the time it was connected to the lead-in tube in the calorimeter. Some was doubtless lost as vapor to fill the tube system itself. The adiabatic expansion of the air in the system could have produced some cooling, though Dieterici states that this was negligible. His data for the evaluation of the heat leaks must be taken as given because of the lack of the details of their computation. There is an uncertainty as to the amount of energy involved in the expansion of the vapor after all the liquid had evaporated. Uncertainties in units can be avoided by using the conversion factor $K=0.27024$ international joules per milligram of mercury as derived above and based on his own determinations of the mean calorie and the Bureau of Standards value of the electrical equivalent of the mean calorie. The 20 experiments thus reduced yield a mean value of 2,490.6 international joules per gram as the latent heat at 0° C. The average deviation of the individual experiments from this mean is 1 part in 847.

(b) GRIFFITHS

Among the earlier determinations of latent heat are those of Griffiths.[30] He reported determinations by a vaporization method under reduced pressures at 30° and 40°. That part of his apparatus in which the thermal changes were isolated and observed consisted essentially of a small oil bath, mechanically stirred and electrically heated, from which water was vaporized. This unit was located inside an iron box containing a large quantity of mercury for thermal ballast and for activating the thermoregulator which automatically maintained the temperature of the surrounding water bath. Temperatures were observed with mercury thermometers carefully calibrated

[29] Ann. Phys., **273**, pp. 494–508; 1889.
[30] Phil. Trans. Roy. Soc. London, **A186**, Pt. 1, pp. 261–342; 1895.

and corrected. Temperature differences between the calorimeter and its surroundings were measured with differential platinum resistance thermometers.

Because of the method of operation adopted—namely, the evaporation of the entire water sample in the calorimeter—the end effects were rather large and troublesome. The energy supplied by the stirrer amounted to about 1 per cent of the total and could be determined to within 1 part in 50 of itself. Griffiths considered this the limiting error in his experiments. The heat leak was on the average about 0.1 per cent of the total energy change involved, a fact which increases the confidence in the final results.

By passing the vapor through 18 feet of silver tube in the oil of the calorimeter proper, the danger of priming was lessened. The possibility that the vapor was superheated was small, and the likelihood of error from this source is not large.

The greatest uncertainty in the reduction of these data to a comparative basis lies in the evaluation of the Clark cells used, in terms of present international volts. Assuming that his cells were made up according to the specifications of the Chicago Congress of 1893, their emf on the present basis becomes 1.4328 [31] international volts. Since Griffiths assigned the value 1.434 volts to his cells at 15°, his results as given must be reduced by 1 part in 600 for conversion to present units. The individual experiments have also been corrected to even temperatures with the aid of the Bureau of Standards values of $\frac{dL}{d\theta}$. The mean results from 7 experiments near 30° and 11 near 40° are

$$L_{30°} = 2{,}426.0 \text{ international joules per gram.}$$
$$L_{40°} = 2{,}400.5 \text{ international joules per gram.}$$

At 30° the individual experiments are in very good agreement, the average deviation from the mean being 1 part in 5,170. At 40° the average deviation from the mean is 1 part in 1,500. In spite of the greater number of experiments at 40°, it appears that the mean value at 30° is probably the more accurate of the two.

(c) A. W. SMITH

A. W. Smith [32] [33] has made determinations of the heat of evaporation of water at five temperatures below 100°. He lays considerable stress on the advantages of the method which he used of allowing quiet evaporation to proceed in a stream of air passing over the surface of the evaporating fluid. In the earlier work the stream of air was allowed to bubble through the water, and the stirring was accomplished in this manner. In these experiments the corrections for thermal leakage were considered negligibly small. In the later experiments which constituted a determination of the latent heat at 100° C., the stirring was accomplished mechanically, and the air did not bubble through the liquid. Experiments were run at various rates and the thermal leakage and pump energy effects were thus eliminated, provided they remained the same in any two experiments which were combined. No correction was applied for the heat effect involved in the expansion of the vapor from saturation pressure down

[31] See footnote 22, p. 489.
[32] Phys. Rev., 25, pp. 145–170; 1907.
[33] Phys. Rev., 33, pp. 173–183; 1911.

to the partial pressure which it exerted in the mixture of air and vapor. In the reports mentioned above there are not sufficient data on the rate of passage of air to permit calculation of this correction. Professor Smith's privately communicated estimate is that, in the experiments at 100° C., the amount of air was not greater than 1 liter for 5 g of water evaporated. If this maximum amount flowed in all the experiments at 100°, the value of the latent heat from each should be decreased by about 1 joule per gram. For all the determinations below 100° where the specific volume of the vapor is relatively large, this correction is doubtless negligibly small.

The measurements of temperature and of power supplied to the calorimeter were sufficiently precise so that they do not limit the accuracy of the final results.

The masses of the water evaporated were carefully determined, but where the samples were as small as 2 or 3 g, as they were in all the earlier experiments, the absolute accuracy becomes more important and is somewhat open to question. No mention is made of the means employed to keep the pump power constant in the stirred calorimeter. A comparison of the results of the individual experiments does not indicate a high degree or reproducibility. For instance, at 100° C., where the consistency is best, the average deviation from the mean is 1 part in 1,000.

A series of four determinations at 100° was made with active boiling and very small flows of air. The average result of this series is 16.7 joules per gram lower than the average of a large series in which the evaporation took place quietly. This low result is explained as being due to the carrying over of unevaporated droplets of water in the air-water stream.

To the reviewer it appears that the danger of priming has often been greatly overestimated. The experimental values for the latent heat are, in nearly every case at hand, independent of the rate of withdrawal of vapor. Mathews [34] records test experiments which indicate the absence of unevaporated droplets in a region above the surface of actively boiling water.

The details of the latter series of experiments by Smith seem too meager to justify his explanation of the low results. For the same reason the formulation of an alternative hypothesis is precluded.

In Table 5 are given the results of Smith's experiments. The data recorded in the report of 1907 have been converted into present international joules by decreasing the values as recorded in terms of the Clark cell at 15° = 1.434 volts by 1 part in 600 in the latent heats, to conform to the value 1.4328 international volts as previously used in this paper. Corrections to the temperatures indicated have been made using the Bureau of Standards values for $\frac{dL}{d\theta}$.

TABLE 5.—*Latent heats from Smith's experiments*

Temperature	Latent heat
°*C.*	*Int. joules/g*
14	2,463.5
21	2,447.6
28	2,431.1
40	2,401.4
100	2,261.6

[34] J. Phys. Chem., 21, pp. 536–569; 1917.

Application of the above-mentioned correction of 1 joule per gram for the superheating of the vapor due to its drop in pressure would reduce the latent heat at 100° to 2,260.6 international joules per gram. Since 1 joule per gram is the maximum to which this correction could have amounted, it can be stated only that according to the best information from Smith's experiments the latent heat at 100° is not less than 2,260.6 international joules per gram.

(d) RICHARDS AND MATHEWS

Determinations of latent heat at 100° by Richards and Mathews [35] and by Mathews [36] using a condensation method were carefully performed. This method possesses the obvious disadvantages that accurate knowledge of the heat capacity of the calorimeter and of the heat content of water is necessary for the reduction of the data. Mathews points out an uncertainty in the heat capacity of his calorimeter equivalent to 1 part in 500 in the latent heat, and calls attention to the fact that the error from this source in the earlier experiments was probably 2 parts in 500. Both papers assume a mean specific heat for water between 20° and 100° of 1.0012 times the specific heat at 21.4°.

Because of so-called premature condensation it was found necessary to extrapolate linearly the values of latent heat plotted against rate of condensation to an infinite rate. Consideration of heat leak alone, which disappears at the infinite rate, forms a more logical basis for such a procedure. It is assumed in the following that the same method of operation and reduction of the data was used by Mathews as that employed in the earlier work. Heat leak was measured experimentally with no flow of steam through the tube connecting the evaporator and the condenser. The value so determined is greater than the true leak during an experiment because of the change in gradient in the connecting tube due to the passage of hot steam through it. On account of the warming of the lower part of the tube thus produced, there is less heat flow down it from the evaporator to the calorimeter.

Let—

Q = the heat transferred to the calorimeter by the condensing steam corrected for everything except the heat leak during the flow period,

A = the heat leak per minute as determined experimentally without flow and as actually used in their reduction of the data,

B = the true heat leak per minute with steam flowing,

L_c = the latent heat as Richards and Mathews calculated it,

L = the value of latent heat as here recalculated,

M = the mass of vapor condensed, and

t = the time during which steam was flowing.

Then

$$L_c = \frac{Q - At}{M} \tag{36}$$

and

$$L = \frac{Q - Bt}{M} \tag{37}$$

[35] J. Am. Chem. Soc., 33, pp. 863–888: 1911.

[36] See footnote 34, p. 496.

Subtracting

$$L-L_c=\frac{(A-B)t}{M} \tag{38}$$

or

$$L=L_c+\frac{(A-B)t}{M} \tag{39}$$

As suggested above, $(A-B)$ is a positive quantity and, over the moderate range of flows used in the experiments, is probably constant. Therefore, the values of L_c as calculated by Richards and Mathews are always lower than the true experimental values by the amount $\frac{(A-B)t}{M}$. The quantity t/M is the time required for condensation of 1 g and is the abscissa of the curve used by them in the extrapolation to infinite flow. As the value of t/M increases—that is, the slower the rate of condensation—the more does L_c deviate linearly from L. It follows that the method of correction to the infinite rate was correct but that the theory of "premature condensation" was superfluous. The question of the deviations from the straight line, which might appear if the flows could be made to approach infinity, does not enter, because the slope only is of importance in the calculation of the results.

The data from the 1911 paper have been recomputed, using the correction to the water equivalent which Mathews later suggested. The data from both sets of experiments have been calculated, using the Bureau of Standards values for the heat content of water.

Because two different vaporizers were employed in the earlier work, the data must be treated in two parts. The results of the recalculation are given in Table 6.

TABLE 6.—*Latent heats from experiments of Richards and Mathews*

Year	Latent heat at 100°, L
	Int. joules/g
1911	2256.5
1911	2253.5
1917	2255.2

It appears that it is the systematic errors, especially the uncertainties in the heat capacities of the calorimeters, which limit the accuracy of the final results of these experiments. Professor Mathews expressed the opinion, in a private communication, that the values of the heat capacities of the calorimeters as used in these calculations are slightly low, but he did not wish to suggest definite numerical changes in them. As a heavier vaporizer was used in the second series of 1911, it may be that the water equivalent in this set should have been corrected by more than the 2 g originally suggested by Mathews.

(e) HENNING

Among the more important determinations of the latent heat of water are those of Henning.[37] [38] His method consisted essentially of

[37] Ann. Phys., 326, pp. 849–878; 1906.

[38] Ann. Phys., 334, pp. 441–465; 1909.

vaporizing the water from a calorimeter in a thermostatted bath and collecting the distillate in a condenser vessel in which the pressure was maintained as nearly as possible equal to the pressure in the calorimeter by means of an atmosphere of inert gas. Determinations at 11 different temperatures between 30° and 180° C. are recorded. His own reduction of these values is summarized in terms of present international units in a brief report published in 1919.[39] This summary gives values of latent heats at 10° intervals from 30° to 180°, obtained by smoothing the experimental values and interpolating with the aid of empirical equations at intermediate temperatures. His own choice of equations to best fit his data is considered adequate and probably better than one made by one less familiar with the work. Among the individual experiments at any given temperature there is rather large variation, but in general the experiments were so numerous that the effect of accidental errors on the final results has been reduced. At the higher temperatures the number of experiments was not so large, and the results are consequently less certain. In the calculation of the mass of vapor which is evaporated but remains in the calorimeter to fill the space left vacant by the removal of water, an approximation is involved, but the error from this source is negligibly small below 180°.

Table 7 shows the values which Henning recorded 1919.

TABLE 7.—*Henning's values of latent heat*

Temperature	Latent heat L	Temperature	Latent heat L
°C.	*Int. joules/g*	*°C.*	*Int. joules/g*
30	2,426.0	110	2,228.5
40	2,403.8	120	2,200.1
50	2,380.8	130	2,170.3
60	2,357.4	140	2,139.8
70	2,333.1	150	2,109.7
80	2,308.0	160	2,079.6
90	2,282.5	170	2,049.4
100	2,255.7	180	2,019.7

(f) JAKOB

Using a method almost identical with that of Henning, but with a new apparatus designed for use at higher temperatures, Jakob,[40] and Jakob and Fritz [41] have continued the latent-heat determinations from 180°. These reports give values through 250°, but the experiments have since been extended to about 310° C. This is an unusually comprehensive undertaking, the final results of which are not yet available. Therefore no attempt is made to include a comparison of such preliminary results of this work as are at hand with those of other experimenters.

(g) CARLTON-SUTTON

The determinations by Carlton-Sutton[42] of the latent heat at 100° deserve special prominence among the other investigations of

[39] Ann. Phys., **363**, pp. 759–760; 1919.
[40] Forschungsarbeiten V. D. I., **310**, pp. 9–19; 1928.
[41] Zeit. d. V. D. I., **73**, pp. 629–636; 1929.
[42] Proc. Roy. Soc. London, **A93**, pp. 155–176; 1916–17.

this important constant. Using a modification of Joly's classical apparatus he measured the heat of condensation of water directly in terms of the mean calorie without any reference to electrical standards. He weighed in place the steam which was condensed on a glass bulb to change its temperature from 0° to 100° C. By performing experiments, first with the bulb nearly filled with pure water and then with the bulb containing a much smaller amount of water, he was able to eliminate its heat capacity as well as many other small factors which would otherwise have appeared as corrections. The difference in the masses of steam condensed in two such experiments is that amount which would change the temperature of a mass of water corresponding to the difference of the two bulb fillings from 0° to 100°.

If the thermal conditions during the two experiments were alike, as was doubtless very nearly the case, no corrections for heat leak are required. Corrections were applied for thermal changes occuring within the bulb and for various other small elements involved in the method. The correction for the thermal changes in the bulb has been independently recomputed and found valid. Although the water in the bulb was heated under a total pressure greater than its vapor pressure, the method of calculation of the correction takes this into account and reduces the data to mean calories defined by the saturation path.

To obtain an accuracy of 1 part in 5,000 requires that the masses be accurate to 0.1 mg. In this factor the author's estimate seems somewhat optimistic. He considers that the formation of a vapor cloud upon admitting the steam into the condensing chamber at 0° is the limiting error. It seems probable that the error in determining the masses is at least as great.

The deviations among the individual determinations indicate a high degree of experimental precision.

The final reported value of 538.88 mean calories, when interpreted in terms of the Bureau of Standards mechanical equivalent of 4.1875 international joules per gram, yields for the latent heat of water at 100° the value 2,256.6 international joules per gram.

IV. INTERCOMPARISON OF EXPERIMENTAL DATA

To aid in the comparison of the data, they are assembled in tables and deviation charts. Deviations from the Bureau of Standards values as bases are plotted to facilitate the comparison of these more recent data with those published previously.

In Table 8 are shown the values of heat content of the liquid, assembled from the previous sections. By the method of computation, the result of Dieterici is made to agree exactly with that of the Bureau of Standards at 100°. Because of the uncertanity in the interpretation of the emf of the Clark cells used by Barnes, his results, expressed in international joules, involve an uncertainty of considerable magnitude. The results of Callendar are omitted in this table, but appear later in the comparisons of the steam tables. The value in the Bureau of Standards column at 303° is extrapolated and is therefore put in parentheses.

TABLE 8.—*Summary of recalculated results on heat content of the liquid*

Temperature, °C	Observer				
	Reynolds and Moorby	Barnes	Dieterici	Jaeger and von Steinwehr	Bureau of Standards
	Int. joules/g.	*Int. joules/g.*	*Int. joules/g.*	*Int. joules/g.*	*Int. joules/g.*
10		42.04		42.07	42.02
15			63.10		62.94
20		83.91	83.82	83.92	83.83
25			104.6		104.72
30		125.66	125.6	125.68	125.59
35			146.2		146.48
40		167.36		167.42	167.34
46			192.2		192.41
50		209.11		209.21	209.11
56			234.2		234.19
60		250.85			250.90
65			271.8		271.84
70		292.64			292.75
78			326.4		326.29
80		334.51			334.66
88			368.2		368.27
90		376.39			376.65
100	418.33	418.30	418.75		418.75
110			461.1		461.0
130			546.6		545.9
156			660.6		657.8
183			776.5		776.0
200			852.6		852.0
221			946.1		947.8
240			1,034.7		1,037.0
259			1,126.7		1,128.9
303			1,348.9		(1,356.3)

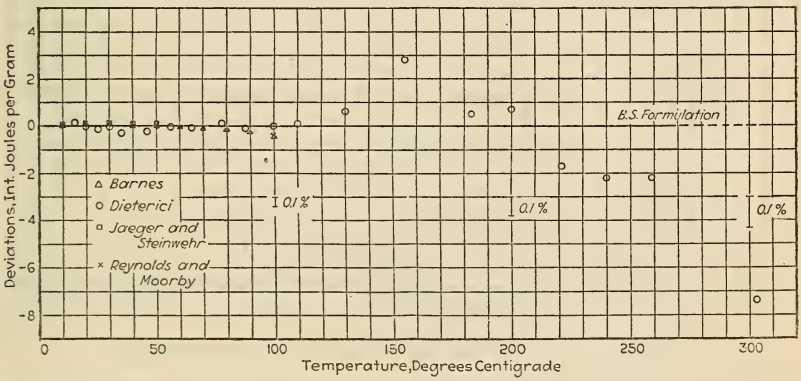

FIGURE 1.—*Deviation chart—heat content of liquid (experimental)*

Figure 1 shows the deviations of the previously published values of heat content of the liquid from the Bureau of Standards values.

In Table 9 are assembled the values of latent heat. Henning's values and those of the Bureau of Standards are calculated from empirical equations which were fitted to the data. The rest of the values are experimental points not smoothed by equations or graphically. The values in parentheses are calculated from the Bureau of Standards latent-heat equation outside the range of the experiments.

TABLE 9.—*Summary of results on latent heat*

Temperature, °C	Observer	Latent heat
		Int. joules/g
0	Dieterici	2,490.6
	Bureau of Standards	(2,494.0)
14	Smith	2,463.5
	Bureau of Standards	(2,463.5)
21	Smith	2,447.6
	Bureau of Standards	(2,447.9)
28	Smith	2,431.1
	Bureau of Standards	(2,432.2)
30	Griffiths	2,426.0
	Henning	2,426.0
	Bureau of Standards	(2,427.7)
40	Griffiths	2,400.5
	Henning	2,403.8
	Smith	2,401.4
	Bureau of Standards	(2,404.9)
50	Henning	2,380.8
	Bureau of Standards	(2,381.6)
60	Henning	2,357.4
	Bureau of Standards	(2,357.9)
80	Henning	2,308.0
	Bureau of Standards	(2,308.8)
90	Henning	2,282.5
	Bureau of Standards	(2,283.4)
100	Henning	2,255.7
	Smith	2,261.6
	Richards and Mathews	2,256.5
	Richards and Mathews	2,253.5
	Mathews	2,255.2
	Carlton-Sutton	2,256.6
	Bureau of Standards	2,257.2
120	Henning	2,200.1
	Bureau of Standards	2,202.7
130	Henning	2,170.3
	Bureau of Standards	2,174.0
140	Henning	2,139.8
	Bureau of Standards	2,144.4
150	Henning	2,109.7
	Bureau of Standards	2,113.8
160	Henning	2,079.6
	Bureau of Standards	2,081.9
170	Henning	2,049.4
	Bureau of Standards	2,048.7
180	Henning	2,019.7
	Bureau of Standards	2,014.1
200	Bureau of Standards	1,939.9
220	Bureau of Standards	1,857.9
250	Bureau of Standards	1,715.6
270	Bureau of Standards	1,603.5

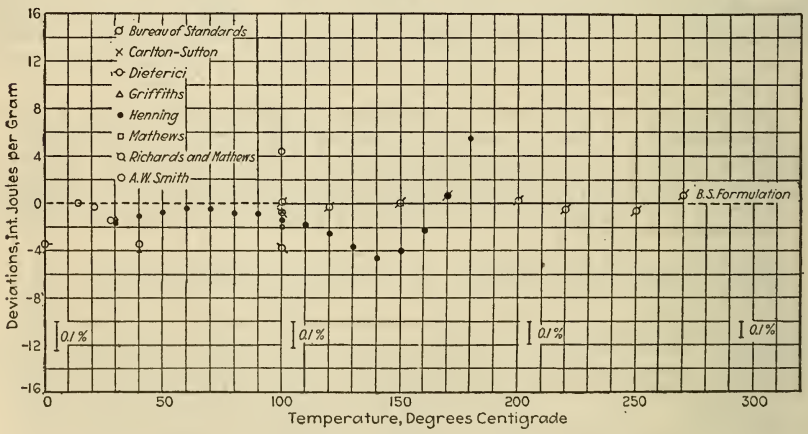

FIGURE 2.—*Deviation chart—latent heat (experimental)*

Figure 2 shows the deviations of the experimentally determined values of latent heat from the Bureau of Standards latent-heat equation.

V. COMPARISON OF STEAM TABLES WITH BUREAU OF STANDARDS RESULTS

For the purposes of this comparison, deviation charts alone are considered adequate. In Figures 3 to 6, which are largely self-explanatory, the base lines are broken in the regions not covered

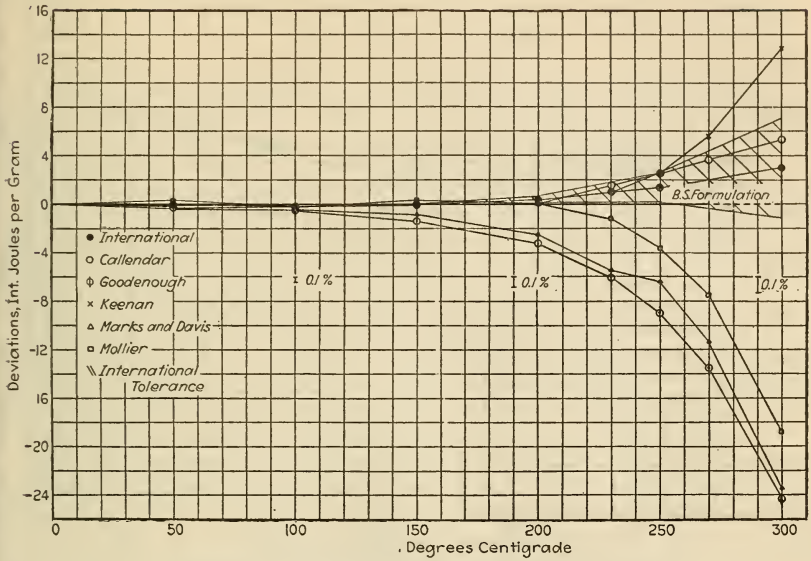

FIGURE 3.—*Deviation chart—heat content of liquid*

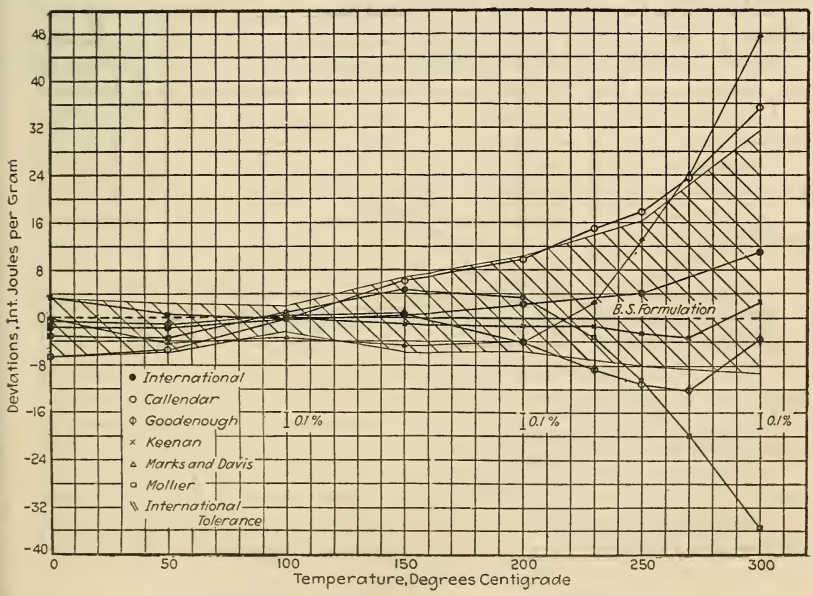

FIGURE 4.—*Deviation chart—heat content of vapor*

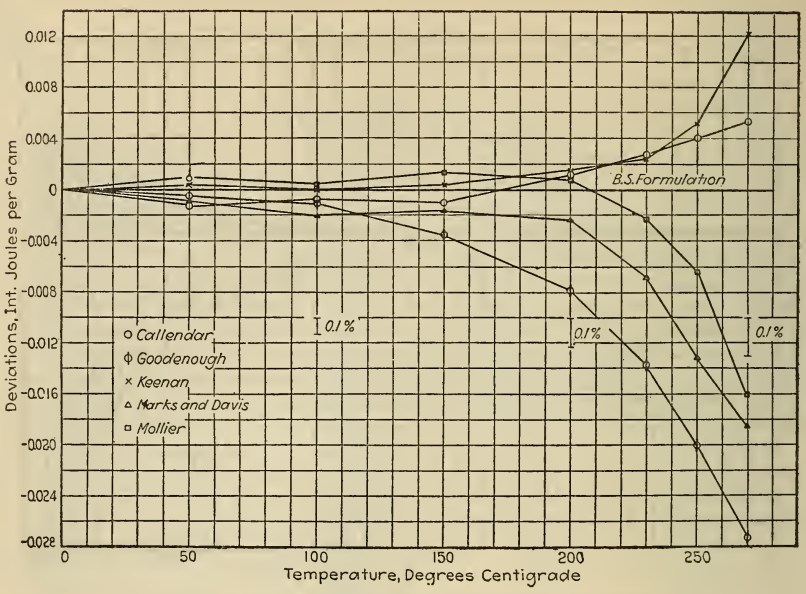

FIGURE 5.—*Deviation chart—entropy of liquid*

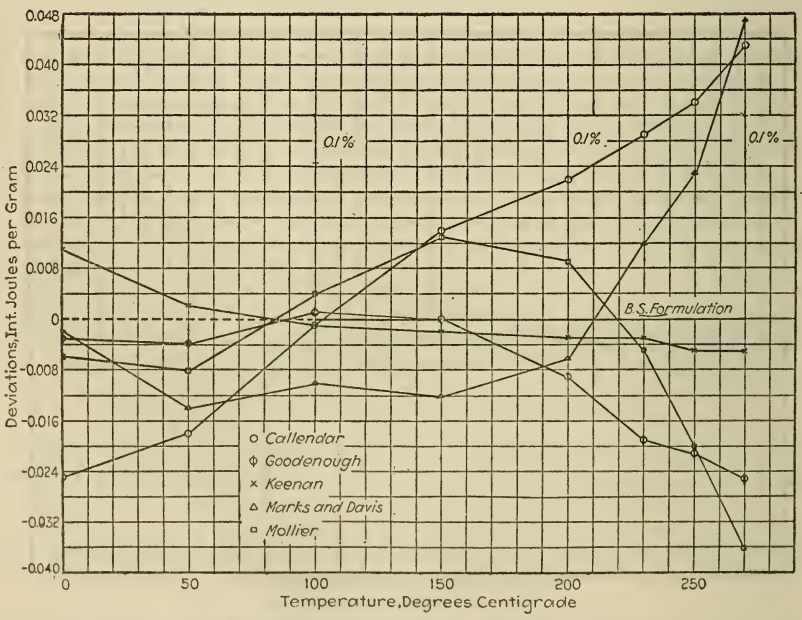

FIGURE 6.—*Deviation chart—entropy of vapor*

by the experiments. The entropy charts are included because values of entropy can be calculated directly from the Bureau of Standards calorimetric measurements.

VI. CONCLUSIONS

For the most part the reviewer believes that the agreement among the experimental results which have been compared is within the limits of the total error involved in the determinations themselves and the conversions to present units.

Referring to the heat-content determinations, the deviation of the Bureau of Standards values from those of Barnes and of Jaeger and von Steinwehr and also of the latter two from each other are, in places, somewhat greater than can be embraced by the estimates which these authors make of their own precision.

The comparisons indicate that the Bureau of Standards latent-heat equation can be used with considerable confidence in the range 0° to 100°, though it was derived solely on the basis of the experiments in the range 100° to 270° and on the classical conception of the vanishing of the latent heat at an infinite rate at the critical point.

The comparison of the steam tables indicates that the divergence in the tabulated properties of saturated water and steam is considerable. None of these tables comes completely within the limits of tolerance of the International Skeleton Steam Table of 1929, and, therefore, none can be called an International Table as specified by the London Conference. A marked improvement is evident in the tables, as more and more data of a precise nature became available for use in the formulations. It is believed that, with the progress in experimental equipment and technique and the mutual understanding of the investigators, the evolution of accurate International Tables of the thermal properties of water and steam has progressed beyond the stage of idealism and that such tables will be a reality before very many years have passed.

WASHINGTON, March 26, 1930.