The Thermodynamic Properties of Water Substance 0° to 150°C PART VI

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Commitments regarding additional research on the properties of water in the region below 200°C made on the occasion of the Third International Conference on Steam Tables in 1934 have been largely completed. Correlation of all new data using James A. Beattie's determinations of the relation of the International temperature scale of 1927 to the thermodynamic scale discloses a high degree of thermodynamic consistency from 0° to 150°C between thermal data, vapor pressures, and equation of state information. The proposed vapor pressures over the temperature range are probably accurate to ±0.002°C. New measurements of vapor pressure over the range are, however, desirable but the ultimate in refinements of temperature control and pressure accuracy should be sought if the indicated discrepancies are to be resolved. Tables of vapor pressure, pressure-temperature derivatives, essential temperature-scale magnitudes, enthalpies, and entropies are given. An equation of state for steam is reported from 0° to 460°C, valid for low pressures and based on the ensemble of volume data and enthalpy pressure coefficients available.

FOLLOWING the publication of tables of the thermodynamic properties of steam in 1936,[1] additional research was undertaken at M.I.T. to obtain experimental confirmation[1a] of the properties of the gaseous phase of water estimated in part by extrapolation in the region below 200°C, a region which had proved virtually impossible of precise exploration by the volume-measuring methods used in the temperature range from 460° to 200°C. The formulation of the volume properties of the gaseous phase in the latter region led to an equation of state $v = F(pT)$,[2] which was used to compute derived properties in the low pressure saturated and super-heated region; justification was secured from the agreement of computed specific volumes between 100 and 200°C with the measurements by Knoblauch, Linde, and Klebe,[3] Joule-Thomson computed coefficients with the measurements of Davis and Kleinschmidt,[4] and other deductions following from thermodynamic relationships.

The additional investigation of steam properties referred to above and begun in 1932[5] soon proved to be of considerable technical difficulty, but a final report was published in 1938.[6] It dealt with the direct determination by a continuous-flow method of the enthalpy variation of steam with pressure from 38° to 125°C. In the same apparatus measurements were also made of the heat capacity in such a way as to lead to C_p^0 values which could be compared with those computed from spectroscopic observations. From the pressure variation of the enthalpy at con-

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* Parts I–V have appeared as follows: Part I. Frederick G. Keyes, "Methods and procedures used in the Massachusetts Institute of Technology program of investigation of the pressures and volumes of water to 460°C," Proc. Am. Acad. **68**, 505 (November, 1933); Part II. Leighton B. Smith, Frederick G. Keyes, and Harold T. Gerry, "The vapor pressure of water," *ibid.* **69**, No. 3, 137 (January, 1934); Part III. Leighton B. Smith and Frederick G. Keyes, "Volumes of unit mass of liquid water and their correlation as a function of pressure and temperature," *ibid.* **69**, No. 7, 285 (April, 1934); Part IV. Frederick G. Keyes, Leighton B. Smith, and Harold T. Gerry, "The specific volume of steam in the saturated and superheated condition together with derived values of the enthalpy, entropy, heat capacity and Joule Thomson coefficients," *ibid.* **70**, No. 8, 319 (February, 1936); Part V. Samuel C. Collins and Frederick G. Keyes, "The heat capacity and pressure variation of the enthalpy for steam from 38° to 125°C," *ibid.* **72**, No. 8, 283 (April, 1938).

[1] J. H. Keenan and F. G. Keyes, *Thermodynamic Properties of Steam* (John Wiley and Sons, Inc., New York, 1936).

[1a] See Mech. Eng. **57**, 710 (1935) for the report on the Third International Conference on Steam Tables. There will be found in this reference the commitments made by the several participating national groups with respect to further research. The contributions by the group at M.I.T. have been partially fulfilled and would have been completed but for the war. An important part of the fulfilled commitment is used in the present paper.

[2] F. G. Keyes, L. B. Smith, and H. T. Gerry, Proc. Am. Acad. Arts and Sci. **70**, 319 (1936).

[3] O. Knoblauch, R. Linde, and H. Klebe, Mitteilung über Forschungsarbeiten auf dem Gebeite des Ingenieurwesens (Julius Springer, Berlin, 1905), Heft 21.

[4] R. V. Kleinschmidt, Mech. Eng. **48**, 155 (1926); H. N. Davis and J. H. Keenan, World Eng. Conf. Reports, Tokyo (1929).

[5] F. G. Keyes and S. C. Collins, Nat. Acad. Sci. **18**, 328 (1932).

[6] S. C. Collins and F. G. Keyes, Proc. Am. Acad. Arts and Sci. **72**, 283 (1938).

stant temperature, important new information bearing on the equation of state was secured confirmatory of the general accuracy of the extrapolations below 200°C referred to earlier.

Another investigation of importance for low pressure properties of water was published by Moser and Zmaczynski[7] in 1939. In this investigation new and highly precise data for the vapor pressure of water from 73.5° to 128.6°C were obtained—very welcome information since no new data had appeared for the region below 100°C since the work of Holborn and Henning (1908) and Scheel and Heuse (1910).[8] Since precision and reproducibility in thermometry have improved notably since 1920, the new low vapor-pressure measurements assist greatly in resolving a difficulty which will be apparent in what follows.

Finally, a highly important series of measurements from 0° to 100°C of the vaporization quantity $vTdp/dT$, or γ, and also the heat capacity of the liquid phase were published in 1939 by Osborne, Stimson, and Ginnings.[9] The new heat measurements are remarkably precise and provide additional information needed to apply the test of thermodynamic consistency to the ensemble of available data.

In addition to the new steam data now available, portions of the extensive thermometric investigations which James A. Beattie and his collaborators have carried out have been published and can be used to fill a gap in our knowledge of the relation of the international temperature scale to the thermodynamic scale. A considerable part of these extraordinarily precise investigations bear on platinum resistance thermometry, gas thermometry, and the position of fixed points in the range zero to the normal boiling point of sulfur. A new fixed point, the N.B.P. of mercury, has been determined[10] and its use shown to be necessary for reproducing the thermodynamic scale by means of the platinum resistance thermometer from 0° to 444.7°C.
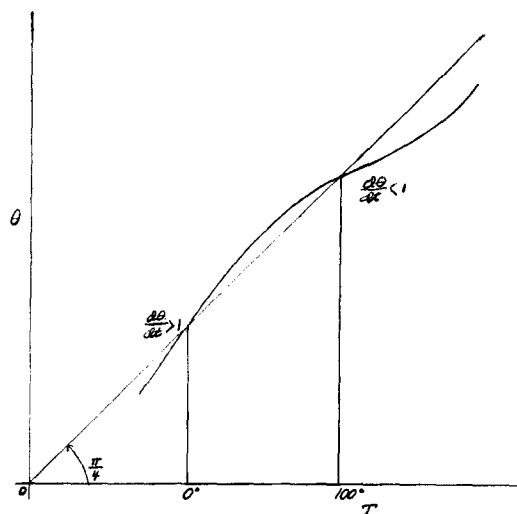

FIG. 1.

The thermometric measurements of more immediate usefulness for the purpose of the present paper have not yet appeared in detail,[10a] namely the results of the comparisons of the indications of the platinum resistance thermometers conforming to the specifications of the international scale (Θ scale) of 1927[11] and the nitrogen gas thermometer at 0, 25, 50, 75, 100, 150, 200, 250, 300, 400°C and the N.B.P. of sulphur. The thermodynamic temperatures (T scale) at these points were determined by extrapolation to zero pressure of the gas-thermometer readings at ice-point pressures 0.6, 0.45, and 0.333 meters of mercury, and also by utilizing virial coefficients for nitrogen.[12] I am grateful to Professor Beattie for his generosity in placing his values of ($T - \Theta$) at my disposal. The use of the latter values in the present paper will illustrate the fundamental importance of a knowledge of the relation of the thermodynamic or T scale to the scale in common use, Θ scale, when applying the test of thermodynamic consistency.

There are two aspects presented in the use of the quantity ($T - \Theta$). These are, first, the direct use in transferring a quantity, for example a measured pressure, from the Θ scale to the ther-

[7] H. Moser and A. Zmaczynski, Phys. Zeits. **40**, 221 (1939).

[8] L. Holborn, K. Scheel, and F. Henning, *Wärmetabellen* (Friedrich Vieweg und Sohn, Braunschweig, Germany, 1919).

[9] N. S. Osborne, H. F. Stimson, and D. C. Ginnings J. Research Nat. Bur. Stand. **23**, 197 (1939).

[10] J. A. Beattie, "The thermodynamic temperature of the ice point," in *Temperature* (Reinhold Publishing Company, New York, 1941), p. 74.

[10a] Edwin Blaisdell and Joseph Kaye, "Location of the normal sulphur and mercury boiling points on the thermodynamic temperature scale," in *Temperature* (Reinhold Publishing Company, New York, 1941), p. 127.

[11] G. K. Burgess, J. Research Nat. Bur. Stand. **1**, 635 (1927).

[12] F. G. Keyes, "Gas thermometer scale, *Temperature* (Reinhold Publishing Company, New York, 1941), p. 45.

TABLE I. v_g cc per gram.

$t°C$	1936 Steam Tables	Goff and Gratch	Percent difference S.T.-G.G.	1934 tolerance cc
40	19546.2	19546.0	+0.0010	±19.0
60	7679.3	7679.9	−0.0078	± 7.7
100	1673.07	1673.13	−0.0036	± 1.7

modynamic or T scale. The second, and often the more important case relates to considerations involving derivatives, $dp/dT = (dp/d\Theta)(d\Theta/dT)$, for example, in thermodynamic equations. The essential features of the situation may be made clear by reference to the diagram, Fig. 1.

The line at $\pi/4$ in the Θ, T diagram defines a set of points for which $\Theta = T$; $d\Theta/dT \gtrless 1$. The curve passing through the fixed points 0 and 100°C is drawn representative of the course of the experimentally determined points for the relation of the international to the thermodynamic scale as determined by Beattie. It will be noted that at some point between 0 and 100°C the course will be parallel to the $\pi/4$ line, or $d\Theta/dT = 1$ although $T \neq \Theta$. The ratio $d\Theta/dT$ is clearly almost, if not exactly, unity at 50°C. The following type of situation often arises. A quantity is measured at 100°C, for example $\gamma = (L + v_f T dp/dT) = v_g T dp/dT$, where L is the heat of evaporation, v_f the specific volume of the saturated liquid, v_g that of the saturated vapor, T the thermodynamic temperature, and p the pressure, which is to be compared with the calculated value of γ. The value of v_g may be assumed given by the equation of state, Eq. (8), namely 1673.27 cc per g, while the value of dp/dT from Table III is 27.122 mm, or 0.0356868 atmos. Accordingly, $v_g T dp/dT$ becomes 2257.38 i.j. (international joules). But $d\Theta/dT$ from Table III is 0.999653 and $v_g \Theta dp/d\Theta = 2258.16$ i.j. The mean observed value (17 observations) from the 1939 published report of Osborne, Stimson, and Ginnings[9] is 2257.32 i.j. It is therefore clear that thermodynamic correlation of vapor pressure data and volume data with calorimetric data without a knowledge of $d\Theta/dT$ would be impossible, even at a fixed point, for data accurate to better than a part in 3000. At 50°C the $d\Theta/dT$ is sufficiently close to unity for every practical purpose. However, Θ differs from T by about

0.01°C; a quantity too small, of course, to be practically significant for some purposes.

The present paper will contain the results of a thermodynamic correlation of the available experimental data on the vapor pressure, the pressure-temperature derivatives, the volumes, heats of evaporation, and enthalpies. The result desired is a set of values of these properties at round temperatures accompanied by an estimate of their accuracy for the temperature range 0° to 150°C. The investigation will provide additional values of steam properties in the range regarded with some uncertainty by the delegates of Great Britain, the United States, Germany, and Czechoslovakia participating in the Third International Conference on Steam Tables held in Washington, New York, and Boston during September 1934.[1a] The skeleton table of properties, Table I of the reference, will have the prospect of being assigned tolerances considerably smaller at such time as a new conference may convene. A brief statement regarding the author's conception of the meaning attached to the concept of tolerances follows. In making the statement, however, it will be understood that what is expressed comprises personal impressions of a former delegate to the Steam Tables Conference. The statement has no official status whatever.

By way of brief review of research on water, the American Society of Mechanical Engineers sponsored a series of investigations of its properties in the early 1920's. The A.S.M.E. Steam Tables Committee, under the able chairmanship of George A. Orrok, very soon solicited the collaboration of British, German, and Czechoslovak colleagues, which resulted in a coordinated research program of international scope. During the three conferences, London 1929, Berlin 1930, U.S.A. 1934, the results of the investigations in progress were reviewed and the work of the conferees culminated in Table I, with assigned tolerances by the end of the 1934 conference.[1a] The tolerances set are *not*, however, definitive estimates of the accuracy* of the quantities to which they are attached. The primary purpose of setting tolerances was to narrow the range of values

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* The connotation attaching to the term "accuracy" used here is that of the relation of an observed magnitude to the "true" value. The term "precision" is taken to mean the reproducibility of observations. An observer may secure precise results which are quite inaccurate.

which would be acceptable in an "international" table of properties. This is a matter of great convenience because prior to the first tables of properties of steam formulated by J. H. Keenan in 1930, the range and accuracy of the fundamental data was too restricted in both accuracy and extent for modern turbine design and test requirements. A table within the tolerances set is known to be of sufficient accuracy for practical purposes, and has the great merit of bringing the interpretation of tests and specifications into a uniform state for ready evaluation. An illustration of the meaning of a tolerance would be the value of the vapor pressure of water at 0°C. Since this is a fixed point on the temperature scale, the temperature assignment is unassailable. The pressures observed at different times by different investigators indicates that the precision may be expressed by the number 4.580 mm±0.001 with a maximum spread of 0.0036 mm. The tolerance assigned, however, is ±0.0044 mm. Another example: the volume of the vapor at 100°C and 1-atmos. pressure is given as 1673.2 ccg^{-1}±1.7 cc, but there is convincing evidence that the accuracy of the number is two or perhaps threefold less than the tolerance assigned.

It will be clear from the foregoing examples of the meaning of the term "tolerance" that it would be misleading to conclude, as has been done recently,[13] that Table I and Table II[1] of the saturation properties below 100°C are inaccurate. Thus the authors state "uncertainties of at least ±0.04 percent at 104°F, ±0.08 percent at 140°F, and ±0.10 percent at 212°F must be assigned to the steam table values of v_g." The values preferred by Goff and Gratch appear in Table 1 below, along with similar values from Table I of the Steam Tables.[1]

The actual volumes listed by Goff and Gratch at 40°C and 60°C are given for pressures on the thermodynamic scale. They have been changed to correspond to pressures on the international scale used for the Steam Tables.

THE VAPORIZATION MEASUREMENTS

The measurements of γ or $v_g T dp/dT$ in the range 0 to 100°C made by Osborne, Stimson, and

Ginnings[9] were carried out in a third, especially constructed, apparatus after 155 measurements[14] at eight temperatures had been made in the first calorimeter in the range from 100° to 270°C, and 214 measurements in a second apparatus at 19 temperatures in the range 100 to 374° (critical temperature 374.13°C). The measurements in the range 0 to 100°C represent a high point in the science and art of heat measurements. They are listed in Table II, the first column of which lists temperatures in degrees C on the international scale. The second column lists the values of $(T-\Theta)$ from Beattie's lower temperature comparisons of the thermodynamic and international scales. The third and succeeding columns give the values of the arithmetic means of the γ-measurements, the average of the sum of the deviations from the average value of γ at each temperature, the square root of the average value of the sum of the squares of the deviations from the arithmetic average values of γ, or the standard deviation s.[15] The sixth column gives values of γ calculated with the empirical equa-

TABLE II. The first column lists centigrade temperatures on the international, Θ-scale, followed by the difference between the international and thermodynamic scales. The third column lists observed mean values of the vaporization quantity $\gamma = v_g T dp/dT$, designated γ_{obs} for water. The fourth and fifth columns contain the average deviation from the means of γ_{obs} and the standard deviation, $s = [\Sigma(x_i - \bar{x})^2/n]^{\frac{1}{2}}$. The smoothed values, or γ_{sm}, are followed by the ratios $(RT/pv)_s$ at saturation.

1	2	3	4 Dev. from weighted mean		5	6	7	8
t_Θ	$(T-\Theta)$	γ_{obs}			s	γ_{sm} Eq. (2)	$(RT/pv)_s$ Eq. (8)	$\gamma_{sm} \times (RT/pv)_s$
0		2500.72	0.124	(5)†	0.137	2500.51	1.00053	2501.78
1	−0.0004	2497.92	0.285	(15)	0.321			
5	−0.0011	2488.34	0.089	(11)	0.100	2488.63	1.00064	2490.25
10	−0.0041	2476.73	0.263	(14)	0.281	2476.80	1.00081	2478.80
15	−0.0060	2464.81	0.262	(6)	0.376	2465.00	1.00100	2467.34
20	−0.0075	2453.36	0.312	(10)	0.382	2453.21	1.00123	2456.15
25	−0.0087	2441.31	0.418	(13)	0.504	2441.41	1.00152	2444.96
30	−0.0097	2429.43	0.335	(11)	0.384	2429.59	1.00184	2433.87
40	−0.0109	2405.87	0.173	(10)	0.206	2405.84	1.00266	2412.01
50	−0.0110	2381.84	0.288	(11)	0.361	2381.88	1.00388	2390.66
60	−0.0098	2357.65	0.202	(8)	0.244	2357.68	1.00523	2369.83
70	−0.0078	2333.25	0.148	(6)	0.170	2333.19	1.00708	2349.60
80	−0.0055	2308.51	0.125	(11)	0.168	2308.40	1.00939	2330.01
90	−0.0028	2283.41	0.088	(4)	0.090	2283.27	1.01225	2311.14
100		2257.32	0.208	(17)	0.301	2257.75	1.01574	2293.28
110	+0.0035					2231.54*	1.01989	
120	+0.0072					2204.75*	1.02484	
130	+0.0115					2177.26*	1.03066	
140	+0.0160					2149.00*	1.03745	
150	+0.0211					2119.87*	1.04529	

† The numbers in parentheses are the numbers of determinations made at each temperature.
* The starred values are from Osborne, Stimson, and Ginnings' Table I, page 265 of reference 17.

[14] N. S. Osborne, H. F. Stimson, J. Research Nat. Bur. Stand. 5, 411 (1930).
[15] F. D. Rossini and W. E. Deming, "The assignment of uncertainties to the data of chemistry and physics," J. Wash. Acad. 29, 416 (1939).

[13] J. A. Goff and S. Gratch, "Low pressure properties of water −160° to 212°F." Am. Soc. Heating and Ventilating Eng. 18, 125 (1946).
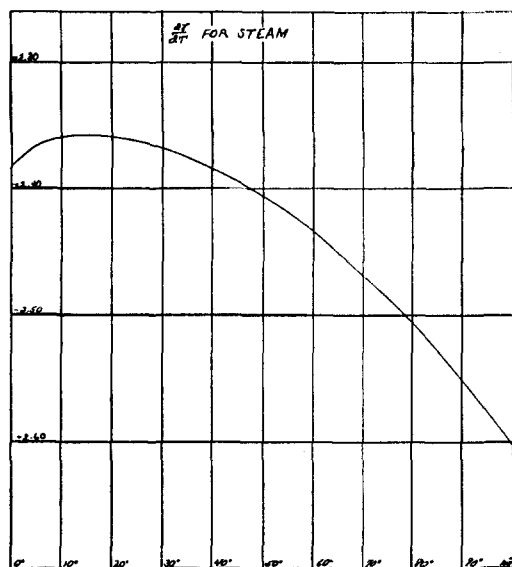
$\frac{d\gamma}{dT}$ FOR STEAM

FIG. 2.

tion (2) obtained by integration of Eq. (1). The seventh column contains values of $(RT/pv)_s$ designating the ratio at the saturation values for the vapor computed from the Eq. (8). The last column contains the product of γ_{sm} and $(RT/pv)_s$.

$$d\gamma/dt = -2.3840 + .00325t - 1.186607 \cdot 10^{-4}t^2$$
$$+ 1.100284 \cdot 10^{-6}t^3 - 4.53677 \cdot 10^{-9}t^4; \quad (1)$$

$$\gamma_{sm} = 2500.51 - 2.3840t + 1.625 \cdot 10^{-3}t^2$$
$$- 3.95554 \cdot 10^{-5}t^3 + 2.7507 \cdot 10^{-7}t^4$$
$$- 8.56354 \cdot 10^{-10}t^5. \quad (2)**$$

The value of γ at 100°C is especially interesting because values obtained from each of the three varieties of apparatus are available. The average measured value from the 1930 measurements is 2258.71 i.j. while 2257.79 i.j. was obtained in 1937, and 2257.32 i.j. in 1939. Relative to the value of the 1939 series we have a drop of 1.39 i.j. and 0.47 i.j. The value 2257.71 i.j. however is listed as preferred in Table I of the 1939 paper;[16] a value near that obtained by the authors by weighting "according to the number of observations and to give the observations of 1930–32 and those of 1937, respectively, one-fourth and one-half the weight of the observa-

** The coefficient of t^5 was altered slightly in the final adjustment.
[16] N. S. Osborne, H. F. Stimson, and D. C. Ginnings, J. Research Nat. Bur. Stand. 23, 261 (1939).

tions" of the 1939 series. The difference between the 1937 mean value at 100°C and the 1939 value, namely 0.47, seems large. Some evidence indicating a preference for the 1939 value will appear later.

In the fourth steam paper of 1936[2] the discussion beginning on page 346 shows that the course of dL/dT, where L is the latent heat of evaporation, exhibits a maximum at about 15°C. An attempt was made at that time to compute the course of the derivative from the following equation:

$$dL/dT = C_{p_g} - C_{p_f} + [(\mu c p)_g - (\mu c p)_f]dp/dT, \quad (3)$$

where cp's are the constant pressure specific heats for the gas and liquid phases, and μ's are the Joule-Thomson coefficients. It was considered doubtful at the time that fully reliable values for differential quantities could be obtained for Eq. (3), and the quantitative aspect of the discussion was postponed. We may now compute the derivatives of $d\gamma/dt = d/dt(L+\beta)$, where $\beta = v_f Tdp/dT$ and correlate the values empirically.[17] Figure 2 shows the course of $d\gamma/dt$ (Eq. (1)).

THE VAPOR PRESSURE EQUATION FOR WATER

An equation for $d\gamma/dt$, having the correct course with temperature, is suitable upon integration in forming an equation for γ_s to be used in the following equation of thermodynamics:

$$v_g T(dp/dT) = \gamma_{sm} = (pv/RT)_s \cdot RT^2(d \ln p/dT),$$

or

$$d \ln p/d\tau = -1/R \cdot \gamma_{sm}(RT/pv)_s = -\gamma_s/R, \quad (4)$$

where τ is the symbol for T^{-1} and $(RT/pv)_s$ differs from unity by the amount of the departure from the ideal gas laws.

The values of γ were measured on the international scale of temperature but since the rate of change of γ with temperature is of the order of 2.4 i.j. per degree, or approximately one part per 1000 of the value of γ, the maximum correction at 50° to express γ on the thermodynamic scale amounts to only 0.024; a quantity perhaps tenfold smaller than the possible error in γ.

[17] To obtain accurate derivatives of a function tabulated at equal intervals of the independent variable, use has been made for many years of a method based on a Lagrangian fourth-degree polynomial, worked out by George Rutledge, Phys. Rev. 40, 262 (1932). The method is as reliable and rapid as it is little known.

The factor $(RT/pv)_s$, a measure of the departure of the saturated volumes from the ideal gas laws, may be regarded as expressed on the thermodynamic scale, provided accurate values can be obtained for the gas-law defect. The value of the ratio increases from 1.00053 at 0° to 1.01574 at 100°C, or to obtain the ratio to a part in 10,000 it is required that the departure from the ideal gas laws be known to one in 5 at 0°, and one in 160 at 100°C. The values of the ratio factor employed were obtained from Eq. (8) using for v_s the values given by Osborne, Stimson, and Ginnings.[18] However after obtaining the final values for the vapor pressure from Eq. (7), final values of $(RT/pv)_s$ were computed and these appear in Table II.

The 1936 equation of state led to a value of the ratio at 100°C 1.0159, the value 1.01574 results from a new equation of state, Eq. (8), obtained by considering all the available evidence. Goff and Gratch,[13] considering only the Collins and Keyes[6] $(\partial H/\partial p)_T$ data in the range 38.94 to 125°C,[13] tabulate values of p and v leading to 1.01583, while at zero degrees their values lead to 1.00048. The ratios deduced from the data of Osborne, Stimson, and Ginnings[16] are, respectively, 1.00056 and 1.01591, using the tabulated volume and pressure of Table II of the reference. The volume at 100°C was deduced, however, from the value of $\gamma=2257.71$ i.j., whereas the value observed in the later series of 17 observations is 2257.32. Moreover the thermodynamic temperature-scale value of Tdp/dT was not employed because of lack of knowledge of $d\Theta/dT$. Using the value of the latter quantity from Beattie's work, namely 0.999653, $(RT/pv)_s$ at 100°C becomes 1.01573.[18]

The values of $\gamma(RT/pv)_s$ given in column 8 of Table II are formed by multiplying the smoothed γ_{sm} values of column 6 by the first approximation values of $(RT/pv)_s$, referred to above. The course of the $\gamma(RT/pv)_s$ values show no minimum or maximum although the curvature is greater in the region 0 to 30° than onward to 100°C. The equation representing the values follows:

$$\gamma_s = \gamma(RT/pv)_s = 2501.78 - 2.3124t$$
$$+ 1.36148 \cdot 10^{-3}t^2 + 8.609233 \cdot 10^{-6}t^3$$
$$+ 2.56 \cdot 10^{-9}t^4. \quad (5)$$

Upon substituting the foregoing equation into the differential equation (4), and integrating, the
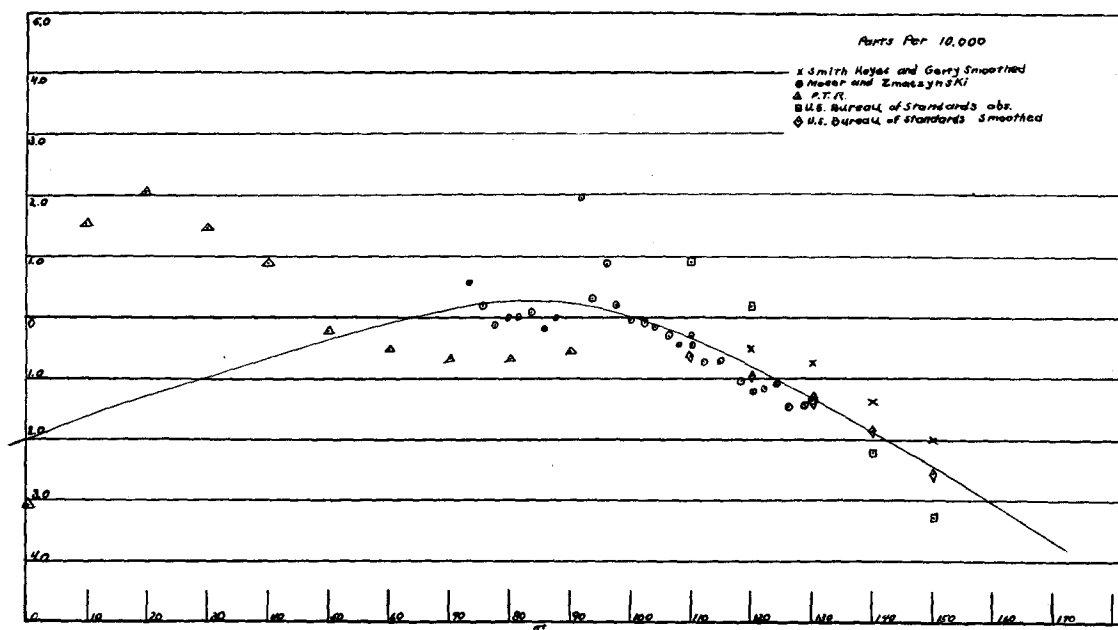

FIG. 3.

[18] The value of v_g at 100°C given by Osborne, Stimson, and Ginnings in reference 16 is 1673.0. The above value of $d\Theta/dT$ needed to employ the thermodynamic equation for calculating v from γ leads to $v_v = 1673.3$ in agreement with the equation of state value.

following vapor-pressure equation is obtained where C_{100} is a constant determined for the pressure 1 atmos. at 100°C.

$$\log p^{mm} = -2892.3693\tau - 2.892736 \log T$$
$$-4.28022 \cdot 10^{-3} T + 2.73522 \cdot 10^{-6} T^2$$
$$+8.03167 \cdot 10^{-10} T^3 + C_{100}, \quad (6)$$

$$C_{100} = +19.2462415.$$

The experimental values of the pressure given in the *Wärmetabellen*,[8] Table 44, 0 to 150°C, were changed to correspond to the thermodynamic scale using the values of $T - \Theta$ from column 2 of Table II. The latter values were also used to transfer the temperatures given by Moser and Zmaczynski[7] to the thermodynamic scale and likewise the temperatures given for the measurements from 110° to 150°C by Osborne, Stimson, Fioch, and Ginnings.[19] The pressure-temperature measurements of Smith, Keyes, and Gerry[20] were made from 150° to 374°C and the pressure values beginning at 100° and extending to 140°C from Table 44 of the *Wärmetabellen* were used in the correlation. The smoothed or correlation values in the latter temperature range were also transferred to the thermodynamic scale along with the smoothed values of Osborne, Stimson, Fioch, and Ginnings. The ensemble of pressure-temperature values were then used in Eq. (6) to compute values of the constant designated C_{obs}, and the differences from the value of the constant C_{100}, designated ΔC, listed. It will be evident that ΔC is equivalent to $\log p_{obs} - \log p^{100}$, where p^{100} signifies pressures computed at temperatures corresponding to pressures p_{obs}, but using always the constant of integration determined at 100°C and 1 atmos. given with Eq. (6).

A graph of the ΔC values *versus* temperature, Fig. 3, clearly indicates a trend. Three pressure values were given great weight in the final correlation of pressures, namely, the defined value $p = 1$ at 100°C, the smoothed values from Osborne, Stimson, Fioch, and Ginnings[19] and Smith, Keyes, and Gerry[20] and the value at zero. The latter pressure was given special study by Dr. Osborne, the result of which he communicated

[19] N. S. Osborne, H. F. Stimson, E. F. Fioch, and D. C. Ginnings, J. Research Nat. Bur. Stand. **10**, 155 (1933).
[20] L. B. Smith, F. G. Keyes, and H. T. Gerry, Proc. Am. Acad. Arts and Sci. **69**, 137 (1934).

to the writer in a letter of February 1934. The letter states: "Thiesen and Scheel in 1900 give the mean value 4.579 mm±.001 at 0°. By examining the observations . . . we find the rounded mean to be 4.5792, and the spread among the individual results to be 0.0036 mm. In 1909 Scheel and Heuse give a mean value of 4.5788 mm±0.0006 with a spread of 0.0030. But these two determinations are not the only ones available. A posthumous paper by K. Prytz was published in *Math. Fys. Meddaleisen Danske Vidensk. Selskab*. **2**, No. 2, 1 (1931), giving an account of a determination of the vapor pressure at the triple point. This temperature of +0.01°C is sufficiently close to the normal ice point to allow very reliable reduction to the same basis as the Physikalische Technische Reichsanstalt. He did not consider his work as final but he gives results of three measurements. When reduced to the zero point they give a mean of 4.5834 mm with a spread of 0.0014 mm. The mean of the three independent determinations giving them equal weight is 4.5804 mm±0.001."

The most recent observed values at 150°C listed below comprise those reported by Osborne, Stimson, Fioch, and Ginnings[19] and Smith, Keyes, and Gerry.[20]

O.S.F.G.

Silver container	3–25–32	4.6954 atmos.
	3–28–32	4.6961
	3–29–32	4.6955
	3–30–32	4.6978
	4– 1–32	4.6972
	7– 1–32	4.6942
	7– 7–32	4.6973
	7–21–32	4.6989
	8– 1–32	4.6959
	Mean	4.6969±0.00136
Smoothed value		4.6977

S.K.G.

Container		
No. 2 machinery steel	7–15–29	4.705 atmos.
No. 2B 18/8 stainless steel	7–30–32	4.6966
No. 2B 18/8 stainless steel	8– 1–32	4.6968
Omitting No. 2 container value, mean		4.6967
Smoothed value		4.6983

The measurement of steam properties in machinery steel even at 150°C was found to be unreliable because of the interaction of water leading to hydrogen evolution. The means of the
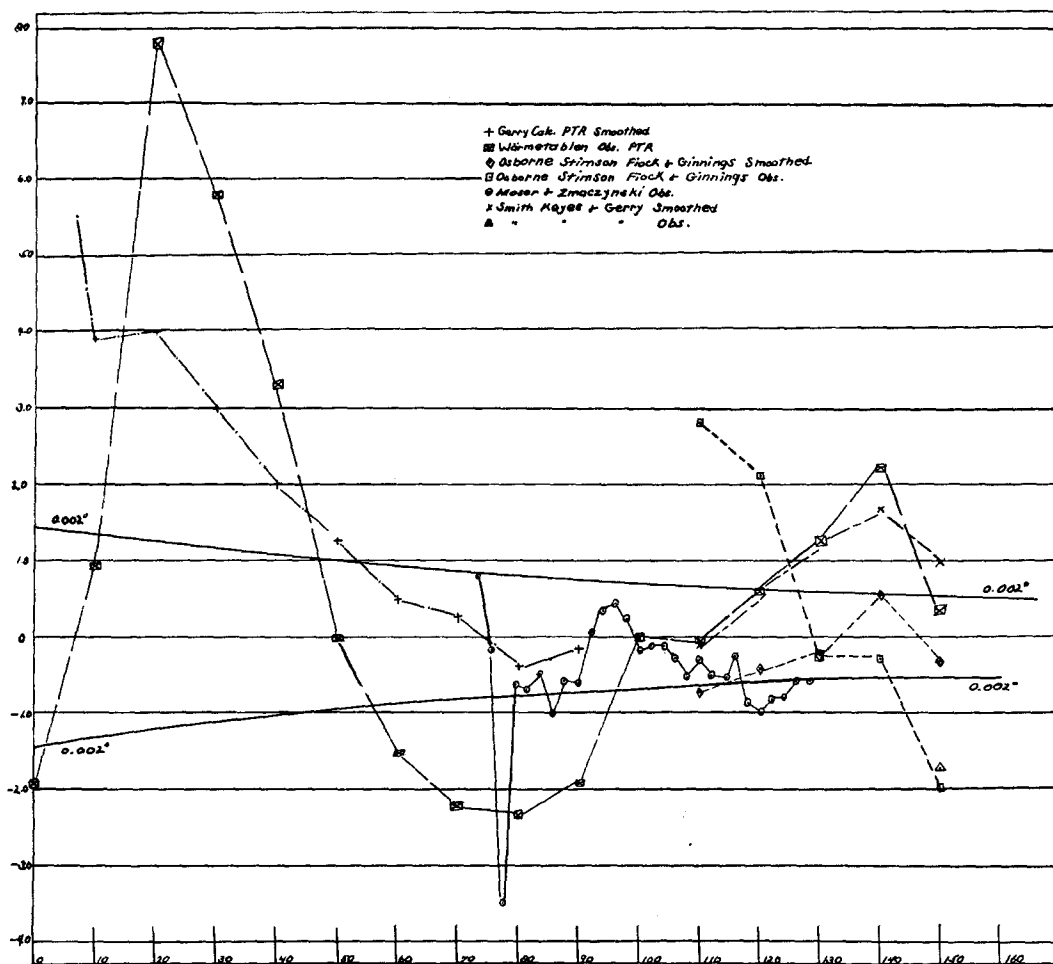
FIG. 4.

$$\mathrm{Log}\,p^{mm} = -(28.92.3693/T) - 2.892736\,\log T - 4.9369728 \cdot 10^{-3}T + 5.606905 \cdot 10^{-6}T^2$$
$$-4.645869 \cdot 10^{-9}T^3 + 3.7874 \cdot 10^{-12}T^4 + 19.3011421$$

two independent values are in good agreement, the pressure difference corresponding to 0.0016°. However, the smoothed values given by Osborne, Stimson, Fioch, and Ginnings and Smith, Keyes, and Gerry, while in agreement to a part in 8000, differ in their mean from the mean of the observed pressures by a part in 3900. This difference may possibly be justified since the smoothing functions used by both groups of observers were arrived at only after many trials and would be expected to result in the "best" (least square) values employing all pressures to the critical temperatures.*** Acting on the assumption that

*** The reader may consult the deviation plots in the original papers (references 19 and 20) showing the departures over the range 100° to 374°C in parts per ten-thousand of the observed from the smoothed values.

the correlation value of the pressure at 150°C is the most accurate, the "correction" curve for the ΔC; t plot passes between the smoothed values. The result is that at 150°C t_T the calculated pressure, Eq. (5), is less than the mean of the smoothed value by a part in 12,000 while the agreement with the smoothed values of Osborne, Stimson, Fioch, and Ginnings and Smith, Keyes, and Gerry is satisfactory below 150°C.

The plot, Fig. 4, shows the deviations of the various values of pressure from the final vapor equation (7). It is clear that the observed points representing Moser and Zmaczynski, and those observed by Osborne, Stimson, Fioch, and Ginnings and Smith, Keyes, and Gerry at 150°C can

TABLE III. "M and Z" refers to the smoothed values of pressure as given by H. Moser and A. Zmaczynski, while the "G and G" refers to the pressures listed by J. H. Goff and S. Gratch. The seventh column lists the smoothed values given by N. S. Osborne, H. F. Stimson, E. F. Fioch, and D. C. Ginnings in 1933. The pressures are expressed on the thermodynamic scale of temperatures from Beattie's $T-\Theta$ values. The eighth column of $d\Theta/dT$ values are deduced from J. A. Beattie's difference formula while the values of dp/dT result from the equation obtained by differentiating Eq. (7). Units of pressure are standard millimeters of Hg.

1	2	3	4	5	6	7	8	9
t_T	Vapor pressure Eq. (7)	Warme-täbellen values corr.*	Steam Table values corr.	M and Z corr.	G and G	O.S.F.G. corr.	$d\Theta/dT$	dp/dT
0	4.580	4.579	4.579		4.5812		1.000422	0.3328
10	9.203	9.212	9.213		9.205		1.000325	0.6167
20	17.529	17.543	17.539		17.531		1.000232	1.0852
30	31.824	31.842	31.833		31.825		1.000144	1.8268
40	55.338	55.356	55.341		55.335		1.000061	2.9504
50	92.558	92.56	92.558		92.555		0.999981	4.5931
60	149.469	149.45	149.452		149.457		0.999906	6.9177
70	233.808	233.76	233.78		233.788		0.999842	10.1121
80	355.310	355.23	355.26	355.282	355.278		0.999771	14.3873
90	525.924	525.82	525.89	525.915	525.891		0.999717	19.9746
100	760.00	(760.00)	760.00	760.00			0.999653	27.122¹
110	1074.44		1074.51	1074.04		1074.43	0.999601	36.091
120	1488.79		1488.90	1488.691		1488.79	0.999553	47.152
130	2025.36		2025.60	2025.113		2025.33	0.999510	60.581
140	2709.24		2709.58			2709.16	0.999472	76.661
150	3568.34		3568.46			3568.05	0.999437	95.675

* The tabulated pressures marked "corr." have been transferred to the thermodynamic scale using column 2 of Table II and column 9 of Table III.

¹ At 100° the value of $dp/d\Theta$ obtained by J. A. Beattie and B. E. Blaisdell, Am. Acad. Arts and Sci. 71, 361, (1937), from measurements of the variation of the steam point with pressure is 27.1313 mm per 1°C. Upon multiplication by $d\Theta/dT$, the value $dp/dT=27.122$ is obtained in agreement with that derived from Eq. (7)

be better represented as a separate ensemble by a straight line passing through 100° and between the latter's points. Sometimes coincidences in data are baffling and this is an example. For the present the pressures computed from Eq. (7) for the vapor pressure of water appear the most reasonable that can be proposed.

$$\log p^{mm} = -2892.3693\tau - 2.892736 \log T$$
$$-4.9369728\cdot10^{-3}T + 5.606905\cdot10^{-6}T^2$$
$$-4.645869\cdot10^{-9}T^3 + 3.7874\cdot10^{-12}T^4$$
$$+19.3011421. \quad (7)$$

Values of pressures computed from the equation are given in Table III. The derivatives dp/dT may be obtained by differentiating Eq. (7) and these values also appear in Table III. Both the pressures and the derivatives calculated correspond to values on the thermodynamic scale of temperature $t_T°$C. Finally, Table III contains observed pressures transferred to the thermodynamic scale which, in the case of Moser and Zmaczynski, have been taken from their own smoothed list of pressure values.

THE RELATION BETWEEN GAMMA-VALUES OBSERVED AND COMPUTED FROM THE VAPOR-PRESSURE EQUATION

Using the values of dp/dT computed from Eq. (7), we may form the quantity $RT^2(d \ln p/dT)$, the equivalent of γ_s which will be designated $\gamma_{s\,calc}$. The values of $\gamma_{s\,calc}$ are listed in Table IV in the second column while the succeeding columns contain in order, the value of γ_{calc}, obtained by dividing $\gamma_{s\,calc}$, by $(RT/pv)_s$ given in the seventh column of Table II, and the values of $\gamma_{sm} - \gamma_{calc}$.

It will be observed that γ_{calc} is larger than γ_{sm} and γ_{obs}, but that at 0°, 50°, and 100°C the agreement with the observed values compare very favorably. The differences are all of the same sign below 90°C which could be interpreted, assuming the measured pressures and the values of $(RT/pv)_s$ to be unassailable, to mean that the γ_{obs} values were affected with a constant error of about 0.3 i.j. However except for the recent measurements of Moser and Zmaczynski below 100°C there is complete lack of data obtained with modern thermometric technique. Indeed this is the weakness of all the older measurements because high purity platinum for thermometers and superior techniques of design and construction are scarcely more than twenty years old. Therefore, before any definitive conclusion can be drawn regarding the differences $\gamma_{sm} - \gamma_{calc}$, new measurements of pressure should

TABLE IV. The value of γ_s calc. results from Eq. (7) and is the quantity $RT^2(d \ln p/dT)$. The third column results from dividing the quantities of the second column by corresponding $(RT/pv)_s$ ratios. The last column exhibits the difference between smoothed γ-values and the γ calc. values of column 3.

t_T	γ_s calc Eq. (7)	γ calc Eq. (7)	$(\gamma_{sm}-\gamma_{calc})$
0	2501.89	2500.56	−0.05
10	2479.09	2477.08	−0.28
20	2456.57	2453.55	−0.34
30	2434.38	2429.91	−0.32
40	2412.57	2406.17	−0.33
50	2391.20	2381.95	−0.07
60	2370.32	2357.99	−0.31
70	2349.99	2333.48	−0.29
80	2330.27	2308.59	−0.19
90	2311.23	2283.26	+0.01
100	2292.94	2257.41	+0.34
110	2275.47	2231.09	+0.45
120	2258.88	2204.13	+0.62
130	2243.27	2176.54	+0.72
140	2228.71	2148.26	+0.74
150	2215.30	2119.32	+0.55

be available. It will be observed that the γ-differences correspond to very small pressure differences.

The course of $(\gamma_{sm}-\gamma_{calc})$ above 100° exhibits a change of sign and of magnitude which enhances the doubts expressed above in discussing the pressures at 150°C. Relative to the values of γ below 100°, those above 100° are, however, probably less accurate. Thus the average deviation for the twenty 1930 measurements at 150°C is 0.59, and s is 0.66.

Regarding the accuracy of the factor $(RT/pv)_s$ consider for example the number at 150°C where an error of one in 4000 would bring the γ-values into agreement. However, this implies an error of one in 180 in the effects of intermolecular force given by the equation of state. For all practical purposes of the moment the result is satisfying and an improved showing must await additional observations of vapor pressure from 0 to 150°C, consistently accurate to a part in 10,000 or better.****

THE ENTHALPY OF STEAM

Values of the enthalpy of steam below 100°C at the time of the 1936 edition of the Steam Tables[1] were obtained by extrapolation as regards the departure of water vapor from the ideal state. The enthalpy equation used was based, except for the gas-imperfection factors, on the values of C_p^0 for gas phase computed by A. R. Gordon[21] with the constant of integration determined from Osborne, Stimson, and Ginnings' value of the enthalpy reported at the Third International Conference on Steam, namely, 2675.35 i.j. The value 2675.33 i.j. is the most recent value listed by Osborne, Stimson, and Ginnings[22] and this value will be used as part of the basis to establish the enthalpy equation.

The equation of state of steam has been under revision during the last year in the form

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**** The best accord in pressure measurements by independent observers is about a part in 10,000, namely, the case of the vapor pressure of CO_2 at zero degrees. The sensitivity of pressure measurements using the pressure balance with electric-contact means of detecting equilibrium can easily be made a part in 20,000. Consistent accuracy to this degree in vapor-pressure measurements will be needed to resolve fully such discrepancies as now exist in the above data.

[21] A. R. Gordon, J. Chem. Phys. **2**, 65 (1934).
[22] N. S. Osborne, H. F. Stimson, and D. C. Ginnings, J. Research Nat. Bur. Stand. **23**, 261 (1939).

TABLE V.

1 t_T	2 B_1 cc/g	3 B_2 cc/g	4 B_3 cc/g	5 $-F_1$	6 $-F_2$	7 $-F_3$ international joules	8 h_g Eq. 10	9 $h_g(ST)-h_g(10)$ parts per 10^4
0	-102.93	-2.89·10⁶	-2.83·10⁷	69.65	238.7		2500.64	+5.9
10	-84.34	-1.52·10⁶	-1.20·10⁷	54.62	78.3	65.14	2519.00	+5.9
20	-70.27	-0.85·10⁵	-0.55·10⁷	43.60	59.91	25.34	2537.26	+5.4
30	-59.42	-4.98·10⁴	-0.27·10⁷	35.42	32.38	11.87	2555.40	+4.4
40	-50.89	-3.04·10⁴	-0.14·10⁷	29.22	18.24	5.65	2573.38	+4.3
50	-44.08	-1.93·10⁴	-7.28·10⁵	24.44	10.95	2.55	2591.17	+3.7
60	-38.57	-1.25·10⁴	-4.06·10⁵	20.70	6.48	1.27	2608.71	+3.3
70	-34.04	-0.85·10⁴	-2.37·10⁵	17.72	4.12	0.676	2625.95	+3.2
80	-30.29	-5.92·10³	-1.42·10⁵	15.33	2.70	0.378	2642.80	+2.8
90	-27.14	-4.21·10³	-0.88·10⁵	13.38	1.81	0.216	2659.26	+2.1
100	-24.48	-3.06·10³	-5.53·10⁴	11.77	1.24	0.126	2675.20	+1.6
110	-22.20	-2.27·10³	-3.57·10⁴	10.43	0.864	0.077	2690.57	+1.5
120	-20.24	-1.71·10³	-2.36·10⁴	9.31	0.617	0.042	2705.31	+1.2
130	-18.54	-1.31·10²	-1.69·10⁴	8.36	0.447	0.031	2719.22	+1.3
140	-17.06	-1.02·10²	-1.08·10⁴	7.54	0.332	0.024	2732.15	+4.0
150	-15.75	-0.81·10³	-0.75·10⁴	6.85	0.249	0.010	2744.76	+1.5

The coefficients of the pressure series for the entropy equations, M_1, M_2, etc., follow from above B and F factors as follows, where τ signifies T^{-1}:

$M_1 = B_1\tau - \tau F_1$ $\qquad F_1 = (\partial B_1\tau/\partial\tau)$
$M_2 = 1/2RB_2\tau^2 - \tau F_2$ $\qquad F_2 = 1/2R(\partial B_2\tau^2/\partial\tau)$
$M_3 = 1/3R^2B_3\tau^3 - \tau F_4$ $\qquad F_3 = 1/3R^2(\partial B_3\tau^3/\partial\tau)$

$p = \varphi(v, T)$. An equation sufficient for all purposes of this paper follows:

$$\log RT/pv = \log\omega/v + \psi\omega/v^2, \qquad (8)$$

where $\omega = v - \beta$ and $\psi = \psi_0 + \psi_1\rho$. For units of cc per gram of steam, standard atmospheres, the quantities are:

$\mathbf{R} = R/M = 4.55465$; $T = 273.16 + t$;
$\beta = 2.061$; $\psi_0 = 1260.17\tau \cdot 10^{7.4238 \cdot 10^4\tau^2}$;†
$\qquad\qquad \psi_1 = 49.97(2.4 + 1286\tau)\tau \cdot \psi_0^3$.

The Eq. (8) may be expanded into the following form sufficiently exact for many purposes:

$$pv = \mathbf{R}T(1 + B_1(p/\mathbf{R}T) + B_2(p/\mathbf{R}T)^2 + B_3(p/\mathbf{R}T)^3), \qquad (8a)$$

where the units are as before, and

$B_1 = (\beta - \psi_0)$; $B_2 = (\beta\psi_0 - \psi_1 - 1/2\psi_0^2)$,
$B_3 = (5/6\psi_0^3 - \psi_0\psi_1 + \beta\psi_1 - 5/2\psi_0^2\beta - \beta^3 + 3\beta^2\psi_0)$.

Table V gives the B coefficients and derivatives of these quantities.

The specific-heat equation at constant pressure for limiting pressure zero will be taken to be as follows:

$$C_p^0 = 1.4722 + 7.7726 \cdot 10^{-4}T + 47.8418\tau(\text{i.j.}),†† \qquad (9)[23]$$

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† The quantities ψ_0 and ψ_1 are given for use with base 10 logs.
†† The factor by which international joules is to be multiplied to obtain absolute joules is 1.0002 in this paper.
[23] Equation 9 results from modifying Eq. 22 of reference 2 based on A. R. Gordon's work (reference 21) by making the correction for "centrifugal stretching" of the water molecule as calculated by E. B. Wilson, Jr.,

and

$$\int C_p{}^0 dT = 1.4722(T-T_0) + 3.8863 \cdot 10^{-4}$$
$$\times (T^2 - T_0{}^2) + 110.16 \log_{10} T/T_0. \quad (9a)$$

The constant of the enthalpy equation, h_0, has been evaluated from the known saturation values at 0° and 100°C in the following way. First using the observed value of γ at 0°, namely, 2500.72, the value of $v_f T dp/dT$ 0.01, and the F factors from Table V, we find $h_0(\gamma_{\mathrm{obs}}\ 0°)$ 2501.14 i.j. Similarly from γ at 100°C, 2257.32 of 1939 and 2257.79 of 1937, we have the mean 2257.56. The quantity $v_f T dp/dT$ is 1.41 and combining $\int C_p{}^0 dT$ with the F factors we find $h_0(\gamma_{\mathrm{obs}}\ 100°)$ 2501.06 i.j.

Second, taking the corresponding smoothed values of γ given in Table II we have h_0, (γ smoothed 0°) $= 2500.93$ i.j. and h_0, (γ smoothed 100°) $= 2501.25$ i.j. The mean of all four values is $h_0 = 2501.09$ i.j. per gram and we may write for the enthalpy of the vapor phase of water the equation following, subject to the convention that the enthalpy of the saturated liquid phase is zero at zero degrees centigrade.

$$h_g = 1801.55 + 1.4722T + 3.8863 \cdot 10^{-4}T^2$$
$$+ 110.16 \log T + F_1 p + F_2 p^2 + F_3 p^3, \quad (10)$$

where F_1, etc. designates the quantities, $(\partial B_1 \tau / \partial \tau)$, $(1/2R) \cdot (\partial B_2 \tau^2 / \partial \tau)$, and $(1/3R^2) \cdot (\partial B_3 \tau^3 / \partial \tau)$.

The enthalpy values computed from Eq. (10) appear in column 8 of Table V, and in the same table column 9 gives the deviation from the values listed in the 1936 Steam Tables. The latter values, although within the 1934 international tolerances, are in every case larger.

The deviation of the enthalpies by Eq. 10 from the 1939 enthalpy assignments by Osborne, Stimson, and Ginnings are within the limits of error of the experimental error of the direct heat measurements from 0° to 100°C, namely, a part in 8000 at most. However above 100°C the Os-

borne, Stimson, and Ginnings values are higher, reaching a maximum of 4.7 parts per 10,000 at 150°C. The results of the γ-measurement series indicate a larger statistical s value relative to the series of 100°C and for lower temperatures, but that they can be in error by as much as a part in 2000 seems doubtful. Actually the agreement between the Osborne, Stimson, and Ginnings assignments and those of the Steam Table improves as higher temperature values are compared, and it may be that a small error in trend of the $C_p{}^0$ is responsible. A revision of the computation of the energy of the water molecule is due, among other items, because of an improved knowledge of the radiation constant C_2. A. R. Gordon used 1.4324 while R. T. Birge lists 1.4385 in 1941.

THE ENTROPY OF THE VAPOR

The entropy equation may be written as follows:

$$s = s_0 + \int_{T_0}^{T} C_p{}^0 dT/T - R \ln p$$
$$- \int_{0}^{p} (\partial v/\partial T - R/p) dp. \quad (11)$$

From Eq. (8a) the last term of the above relation may be evaluated in the form $M_1 p + M_2 p^2 + M_3 p^3$, and the M coefficients obtained simply from the tabulations of Table V for B and F by use of the relationships at the foot of the table. The final equation follows where s_0 is obtained from the value of s "observed" at 0°C and 100°C, the convention being adopted that s for the saturated liquid is zero at 0°C.

$$s = -1.4988 - 1.06243 \log p + 3.38987 \log T$$
$$+ 7.7726 \cdot 10^{-4} T - 47.8418\tau$$
$$+ M_1 p + M_2 p^2 + M_3 p^3 \cdots. \quad (12)$$

The agreement of the entropy values computed from the foregoing equation with the tabulated values of the entries in Table I of the Steam Tables is 4.5 parts per 10,000 at 0°, 1.4 parts at 100°, and 0.6 parts at 150°C. The agreement with the assignments of Osborne, Stimson, and Ginnings is excellent, the greatest deviation amounting to 2.5 parts per 10,000 at 150°C.

J. Chem. Phys. **4**, 526 (1936); a calculation confirmed later by a recomputation [C. C. Stephenson and H. O. McMahon, J. Chem. Phys. **7**, 614 (1939)] of the rotational partition function from Dennison, Ginsburg, and Weber's data, Phys. Rev. **52**, 160, (1937). The relation 1 i.j. = 1.0002 ab.j. has been used.