Thus, there should be a value of K for which a plot of the left side of equation 11 *versus* m gives a straight line of slope b_1. Plots of this equation for several values of K are given in Fig. 2. In general, straight lines of slope 0.07 to 0.08 are obtained for large values of m. However, it may be noticed that large deviations from linearity are obtained at small values of m for $K > 3$. These deviations are opposite to those expected for dissociation of UO_2F_2 into ions, and hence the values of K for which such concavity downward occurs must be considered too large. Best linearity throughout the whole range of m is found for $K = 1.5$.

In Fig. 3 a comparison of the experimental values of θ/m with a theoretical curve calculated on the assumption $K = 1.5$ and $b_1 = 0.07$ is given. This theoretical curve was calculated by the use of the equation

$$\frac{\theta}{1.86m} = \frac{-55.5}{RT}\frac{\mu_s^e}{m} - = \frac{m_1 + Km_1^2}{m} + \frac{2.303\ b_1m}{2} \qquad (12)$$

where μ_s^e is the excess of the chemical potential of the solvent over its standard chemical potential and is defined by the equation $\mu_s^e = \mu_s - \mu_s^0$. Equation 12 can be derived as follows: let μ_A^e be the analogous excess chemical potential for the solute, then

$$\mu_A^e/RT = \ln m_1 + 2.303\ b_1m \qquad (13)$$

Use of the Gibbs–Duhem equation yields

$$\frac{1}{RT}\,\mathrm{d}\,\frac{\mu_A^e}{\mathrm{d}m} = \frac{\mathrm{d}m_1}{m_1\,\mathrm{d}m} + 2.303\ b_1 = \frac{-55.5}{mRT}\,\mathrm{d}\,\frac{\mu_s^e}{\mathrm{d}m} \qquad (14)$$

Rearranging this equation, integrating, and substituting θ in terms of μ_s^e, with neglect of the higher terms in θ, yields equation 12.[18]

While the calculated curve clearly reproduces the general features of the experimental data, agreement is not obtained within experimental error and various attempts to fit it by different choices of the two parameters K and b_1 do not yield significantly better agreement. It is believed that the deviations are probably primarily due to partial dissociation of UO_2F_2 into ions at low m and changes of K, b_1 and b_2 with temperature. Nevertheless the agreement is sufficiently good to show that uranyl fluoride exists in solution primarily as neutral species, tends to dimerize with a constant K approximately equal to 1.5, that the logarithms of the activity coefficients of both the monomeric and dimeric species vary approximately linearly with m and that the corresponding proportionality constants are *ca.* 0.07 and 0.14.

Acknowledgment.—The authors are greatly indebted to Professor George Scatchard and to Dr. R. W. Stoughton for a number of very valuable discussions.

[18] See also ref. 16, p. 286.

OAK RIDGE, TENNESSEE

[CONTRIBUTION NO. 23 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

A Calorimetric Determination of the Vapor Heat Capacity and Gas Imperfection of Water

BY J. P. MCCULLOUGH, R. E. PENNINGTON AND GUY WADDINGTON

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Values of the heat capacity of water vapor were obtained at several pressures in the range $^1/_8$ to 1 atmosphere at each of five temperatures between 361 and 487°K. It was found that the vapor heat capacity is not a linear function of pressure. Experimental values of $(\partial C_p/\partial P)_T$ and the volume data of Osborne, Stimson and Ginnings were used to obtain empirical expressions for the second and third virial coefficients, B and C, of the equation of state, $PV = RT + BP + CP^2/RT$. By integrating the expression for $(\partial C_p/\partial P)_T$ in terms of this equation of state, an equation for the vapor heat capacity as a function of temperature and pressure was derived. In the range of temperature and pressure of the experiments, the equation represents the calorimetric data to within ±0.1% and values of C_p° computed from spectroscopic and molecular structure data within ±0.05%.

Although water has been the subject of intensive thermodynamic investigation, certain important properties of the vapor have not been determined experimentally. Accurate measurements have been made of the latent heat of vaporization,[1] enthalpy of the saturated liquid and vapor,[1] vapor pressure,[1,2] vapor heat capacity at high temperatures and pressures,[3] Joule–Thompson coefficient[4] and specific volume[5] of the vapor. These data have been correlated by means of a single equation of state.[2,6] The variation of the vapor heat capacity with pressure at pressures below atmospheric has not been studied previously. In addition, the indirect experimental determination of C_p° by Collins and Keyes[7] at and below 125° resulted in values 0.3% higher than those computed from spectroscopic and molecular structure data.[8] It was felt that further verification of this important property was desirable. For these reasons the heat capacity of water vapor was investigated at pressures from $^1/_8$ to 1 atmosphere at each of five temperatures between 361 and 487°K., using experi-

[1] N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939) (original references cited there).

[2] F. G. Keyes, *J. Chem. Phys.*, **15**, 602 (1947) (original references cited there).

[3] (a) O. Knoblauch and W. Koch, *Mech. Eng.*, **51**, 147 (1929); (b) W. Koch, *Forsch. Gebiete Ingenieurw.*, **3A**, 1 (1932).

[4] R. V. Kleinschmidt, *Mech. Eng.*, **48**, 155 (1926).

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

[6] J. H. Keenan and F. G. Keyes, "Thermodynamic Properties of Steam," John Wiley and Sons, Inc., New York, N. Y., 1936.

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

[8] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

mental techniques developed in this Laboratory for studying the thermal properties of hydrocarbons. The results of the calorimetric investigation are reported in this paper. Also presented is an equation of state employed to correlate the thermal data and the calculated values of C_p°.

Experimental

The Material.—The water used in this investigation was deionized and then distilled in the presence of $KMnO_4$. The amount of impurity remaining after this treatment would not have a detectable effect on the vapor heat capacity measurements.

The Apparatus and Method.—The measurements of the heat of vaporization and vapor heat capacity of water were performed with the flow calorimeter system that has been described in earlier publications from this Laboratory.[9] A metal cycling vaporizer (similar in principle to the glass vaporizer mentioned in ref. 9) was used for this investigation. The vaporizer heating element was sheathed by small diameter copper tubing to prevent contact with the liquid. Glass thread was wrapped around the sheath to promote the extremely steady boiling that is required.

Since reference 9a contains a detailed description of the experimental procedure, only a brief outline of the method will be given here.

The steady stream of vapor generated in the vaporizer, after passing through the flow calorimeter, is condensed and the liquid is returned to the vaporizer. A relationship between the power input of the vaporizer heater and the vapor flow rate is obtained by diverting the vapor into a cooled receiver for a measured time interval and weighing the condensate produced by a measured energy input. By applying small corrections to the proportionality thus obtained, the heat of vaporization may be computed.[9a]

The calorimeter, designed so that only radiation heat losses are significant, contains an electrical heater and three platinum resistance thermometers, one upstream from the heater and two downstream. The heat capacity of a vapor is determined by passing it through the calorimeter at a known rate of flow, *F*, and observing the temperature rise, ΔT, when a measured power input, *W*, is maintained by the calorimeter heater. The vapor heat capacity is then given by the relationship

$$C_p = W/F\Delta T - k/F = C_p(\text{app.}) - k/F$$

where *k* is related to the heat loss from the calorimeter to its surroundings. For a particular mean vapor temperature and a constant ΔT, *k* is essentially independent of flow rate. Hence, C_p may be evaluated by plotting the apparent heat capacity [C_p (app.)], obtained from experiments at several flow rates, against $1/F$ and extrapolating the resulting straight lines to $1/F = 0$. Independent values of ΔT are obtained with the two downstream thermometers. The corresponding results for C_p usually agree within 0.05%.

The Heat of Vaporization.—Accurate heat of vaporization data for water have been published by Osborne, Stimson and Ginnings.[1] In order to determine if the flow rates produced by the cycling vaporizer were consistent with the data of these investigators, the heat of vaporization of water was determined at two temperatures. The results of five measurements at 65.00° and three at 100.00° were 10,108 ± 3 and 9714 ± 5 cal. mole^{-1}, respectively, where the uncertainties given denote the maximum deviation of experimental results from the mean. These values differ from those of Osborne, *et al.*, by +0.09 and −0.03%, respectively. The greater discrepancy at 65.00° is probably a result of unusually large boiling temperature fluctuations caused by the condensation conditions that prevailed during the heat of vaporization measurements. Since steady boiling temperatures indicated steady flow rates during the vapor heat capacity measurements, the reliable data of Osborne, *et al.*, were employed to compute rates of flow at all boiling temperatures.

The Vapor Heat Capacity.—Values of the heat capacity of water vapor were obtained at several pressures in the range $^1/_8$ to 1 atmosphere at each of five temperatures between 361 and 487°K. The results are presented in Table I and Figs. 1 and 2. It is believed that the accuracy uncertainty of these data should not be greater than ±0.2%.

The plots of C_p *vs.* *P* shown in Fig. 1 demonstrate that the heat capacity is not a linear function of pressure. This fact necessitated the use of a more complex equation of

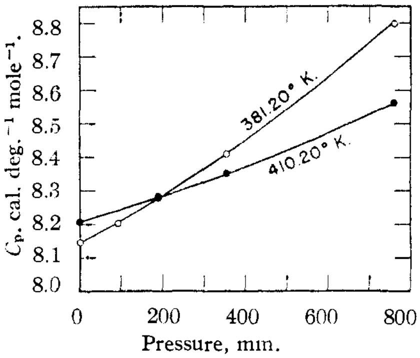

Fig. 1.—The pressure dependence of the vapor heat capacity (diameter of circles = 0.2% of C_p).

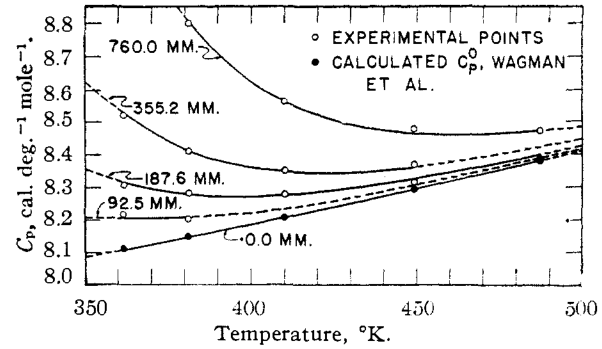

Fig. 2.—The vapor heat capacity of water (diameter of circles = 0.2% of C_p).

TABLE I

THE VAPOR HEAT CAPACITY OF WATER IN CAL. DEG.$^{-1}$ MOLE^{-1}

1 cal. = 4.1833 int. j.; 0°C. = 273.16°K.; mol. wt. 18.016

T, °K.	*P*, mm.	C_p (obsd.)	C_p (equ. 4)
361.80	355.2	8.520	8.529
	188.2	8.308	8.317
	92.5	8.218	8.206
	0.0	*8.113*[a]	8.107
381.20	760.0	8.800	8.807
	355.2	8.410	8.412
	188.2	8.282	8.278
	92.5	8.203	8.208
	0.0	*8.148*[a]	8.146
410.20	760.0	8.565	8.563
	355.2	8.351	8.349
	188.2	8.278	8.277
	0.0	*8.206*[a]	8.206
449.20	760.0	8.477	8.462
	355.2	8.370	8.360
	188.2	8.315	8.325
	0.0	*8.292*[a]	8.291
487.20	760.0	8.471	8.471
	188.2	8.385	8.398
	0.0	*8.383*[a]	8.380

[a] Interpolated from the statistically calculated values of C_p° listed by Wagman, *et al.*, in Table VII, ref. 8.

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(9) (a) Guy Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **69**, 22 (1947); (b) Guy Waddington and D. R. Douslin, *ibid.*, **69**, 2275 (1947).

state than that used to correlate the effects of gas imperfection on the vapor heat capacity of hydrocarbons and related substances.[9,10] The treatment of gas imperfection adopted for water vapor will be discussed in the next section.

The experimental heat capacity results at each temperature were extrapolated to zero pressure by fitting equations quadratic in pressure ($C_p = C_p^\circ + xP + yP^2$) to the data by means of least squares adjustments. The values of C_p° so obtained differed from those of Wagman, *et al.*,[8] by 0.006 and 0.002 cal. deg.$^{-1}$ mole^{-1} at 381.20 and 410.20°K., respectively, but were 0.3% higher than the theoretical result at 361.80°K. and 0.2 to 0.3% lower at the two highest temperatures. The larger differences are probably the result of uncertainties in extrapolation caused by the large curvature in the plot of C_p *vs.* P at 361.80°K. and by decreased precision of the experimental data at the two highest temperatures. Because close agreement was found between the "observed" and calculated values of C_p° at 381.20 and 410.20°K., where the reliability of the extrapolation to zero pressure is greatest, the values of C_p° listed by Wagman, *et al.*, were employed instead of the extrapolated results in the correlation that follows.

Gas Imperfection and Correlation of the Heat Capacity Data.—The pressure variation of the vapor heat capacity, as an effect of gas imperfection, may be related to an equation of state for the vapor. Since no available equation of state represents the observed heat capacity of gas imperfection within the probable accuracy uncertainty of the data, an expression of convenient form was employed to correlate the present calorimetric data with the values of C_p° of Wagman, *et al.*,[8] and the volume data of Osborne, *et al.*[1]

A virial equation of state of the following type was assumed

$$PV = RT + BP + CP^2/RT \qquad (1)$$

with $B = b + c\,\exp(a/T)$ and $C = \beta + \gamma\,\exp(\alpha/T)$.

In terms of this representation the vapor heat capacity may be expressed in the form

$$C_p = C_p^\circ - \int_0^P T(\partial^2 V/\partial T^2)_P \mathrm{d}P$$
$$= C_p^\circ + xP + yP^2 \qquad (2)$$

where x and y are pure temperature functions of the virial coefficients, B and C. The functions x and y were evaluated at each of five temperatures by fitting eq. (2) to the experimental vapor heat capacity data *and* the values of C_p° tabulated by Wagman, *et al.*,[8] by means of least squares adjustments. The constants a, c, α, β and γ of (1) were evaluated from these results for x and y by an iterative process in which added weight was given to the data obtained at those temperatures where the measurements were most reliable. The constant b in the expression for B was determined with the aid of the accurate volume data of Osborne, *et al.*[1] In this manner the following equations were obtained for the virial coefficients

$$B = -341 - 0.3807\,\exp(2300/T),\ \text{cc. mole}^{-1}$$
$$C = 6.98 \times 10^6 - 7.589 \times 10^4\,\exp(1600/T),\ \text{cc.}^2\ \text{mole}^{-2} \qquad (3)$$

The above method for obtaining expressions for B and C is such that these quantities are not directly comparable to those presented by Keyes[2] or by Hirschfelder, McClure and Weeks.[11] The equation for B has the same form as that given by Hirschfelder, *et al.*,[11] and if the same physical significance is attached to the constants of the expression, the above value of a (2300 deg.) corresponds to an unusually large energy of association of about 4600 cal. mole^{-1}, presumably as a result of the formation of hydrogen bonds by the water vapor dimer.[12] Using Keyes' data for B,[2] Rowlinson[13] obtained values for the hydrogen-bond strength in water vapor of 4440 or 4980 cal. mole^{-1}, depending upon the representation employed for B. The uncertainty in the present value for the energy association is large enough to include both of those given by Rowlinson, since a is quite sensitive to errors in $(\partial C_p/\partial P)_T$ at zero pressure, and the latter quantity cannot be determined with high accuracy by the experimental methods used.

By utilizing eq. (3) to obtain expressions for x and y, the following equation for the vapor heat capacity of water was obtained

$$C_p = C_p^\circ + \{(64.17/T) + 0.0558\}\{\exp(2300/T)\}\{P/T^2\} - 3.57 \times 10^{-3}\{P^2/T^2\} + \{(49.64/T) + 0.1241 + 3.878 \times 10^{-5}T\}\{\exp(1600/T)\} \times \{P^2/T^3\},\ \text{cal. deg.}^{-1}\ \text{mole}^{-1} \qquad (4)$$

where $C_p^\circ = 7.639 + 6.433 \times 10^{-4}T + 1.800 \times 10^{-6}\,T^2$, cal. deg.$^{-1}$ mole^{-1}; T is in °K.; and P is in mm. Examination of Table I and Fig. 2 shows that eq. (4) represents the experimental data to approximately ±0.1% and the values of C_p° computed from spectroscopic and molecular structure data to about ±0.05%. One experimental point at 449.20°K. deviates by 0.2%. The curves drawn in both Figs. 1 and 2 were calculated with the aid of eq. (4).

Although the calorimetric data were precisely correlated with the use of eqs. (1) and (3), these equations are essentially empirical and are not expected to be reliable beyond the range of temperature and pressure of the experiments (323 to 487°K., 0 to 760 mm.).

Discussion

The results of the foregoing correlation indicate that the experimental data of the present investigation are consistent with the C_p° values of Wagman, *et al.*[8] It is also important to examine the consistency of the data with the equation of state of Keyes[2] which resulted from a careful evaluation and correlation of existing volume and thermal data for water. In Table II, columns I to IV, are given C_p° values obtained by reducing each C_p(obsd.) of Table I to C_p° by subtraction of the appropriate $(C_p - C_p^\circ)$ term calculated from Keyes' equation of state.[14] Inspection of Table II reveals two trends in the computed values of C_p° in columns I to IV. First, at each temperature, there is a trend in the several derived values of C_p° such that those obtained from C_p^1 (column I) are lower than

TABLE II

COMPARISON OF IDEAL GAS HEAT CAPACITIES IN CAL. DEG.$^{-1}$ MOLE^{-1}

	$C_p^{\circ a}$						C_p°
T, °K.	1 atm.[b] I	1/2 atm.[b] II	1/4 atm.[b] III	1/8 atm.[b] IV	Mean V	C_p° (Keyes)[c] VI	(Wagman)[d] VII
361.80	...	8.084	8.095	8.118	8.099	8.105	8.113
381.20	8.112	8.124	8.138	8.135	8.127	8.139	8.148
410.20	8.179	8.183	8.191	...	8.184	8.195	8.206
449.20	8.269	8.276	8.266	...	8.270	8.278	8.292
487.20	8.343	...	8.354	...	8.348	8.365	8.383

[a] Calculated from experimental values of C_p and values of $(C_p - C_p^\circ)$ computed as described in footnote 14. [b] C_p° computed from C_p (obsd.) at the approximate pressure indicated. [c] Computed with the aid of eq. 8, ref. 15. [d] Interpolated from Table VII, ref. 8.

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(10) D. W. Scott, Guy Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

(11) J. O. Hirschfelder, F. T. McClure and I. F. Weeks, *ibid.*, **10**, 201 (1942).

(12) C. F. Curtiss and J. O. Hirschfelder, *ibid.*, **10**, 491 (1942).

(13) J. S. Rowlinson, *Trans. Faraday Soc.*, **45**, 974 (1949).

(14) The relationship employed in these calculations was $C_p - C_p^\circ = -\int_0^P T(\partial^2 V/\partial T^2)_P\,\mathrm{d}P$, where $(\partial^2 V/\partial T^2)_P$ was obtained from Keyes' data by numerical differentiation of the F factors in his Table V, ref. 2. Direct differentiation of eq. (8a), ref. 2, gave the same result at 361.80°K. as the numerical method.

In using Keyes' Table V, cognizance was taken of the error in sign of the M coefficients in eq. (12), ref. 2, referred to by Halford [J. O. Halford, *J. Chem. Phys.*, **17**, 405 (1949)]. Furthermore, attention is directed to the fact that for use in eq. (8a) and in the expression for the virial coefficients, the equations given for ψ_0 and ψ_1 are to be multiplied by ln 10 and $1/(\ln 10)^2$, respectively.

The figures for F_3 in Table V were found to be in cc.-atm. g.$^{-1}$ atm.$^{-3}$, and on communication with Professor Keyes, we have been informed that the original computation sheets show failure to convert the original F_3's in cc.-atm. g.$^{-1}$ atm.$^{-3}$ to int. j. g.$^{-1}$ atm.$^{-3}$ by multiplication by the factor 0.10131.

those from $C_p^{\frac{1}{2}}$ (column II), etc., *i.e.*, the larger the correction for gas imperfection, $(C_p - C_p^\circ)$, the lower is the value obtained for C_p°. Second, the spread of the computed values of C_p (columns I to IV) diminishes from 0.4% at 361.80°K. to 0.1% at 487.20°K., just as the value of $(C_p - C_p^\circ)$ decreases exponentially with temperature. Since the internal consistency of the experimental data is probably about ±0.1%, and is certainly better at the lower temperatures than at the higher, the two trends noted in the results shown in Table II are believed to be due to the fact that the values of $(C_p - C_p^\circ)$ computed from Keyes' equation of state are slightly large.

Table II also contains values of C_p° calculated with the aid of Keyes' semi-empirical equation for the enthalpy of ideal water vapor.[15] The values of C_p° (mean), obtained by averaging columns I to IV, agree better with the results obtained from Keyes' enthalpy relationship [C_p° (Keyes)] than with the values of Wagman, *et al.* [C_p° (Wagman)]. (It should be noted that the differences between C_p° (Keyes) and C_p° (Wagman) are 0.2% or less in this temperature range.) The present data, then, cannot be employed to substantiate unambiguously either set of calculated C_p°'s. However, since Keyes' equation of state does not represent the present calorimetric data within its precision, the agreement of C_p° (mean) of Table II with C_p° (Keyes) is probably fortuitous. The excellent consistency obtained by the method of correlation described in the previous sections (see Table I, Figs. 1 and 2) favors the C_p° values of Wagman, *et al.* New calculations of the thermodynamic functions of water are to be made in another laboratory and must be awaited for a definite resolution of these relatively minor differences.

TABLE III

THE ENTROPY, IN CAL. DEG.$^{-1}$ MOLE^{-1}, OF GAS IMPERFECTION AT SATURATION PRESSURE

T, °K.	P, mm.	$(S^* - S)$obsd.[a]	$S^* - S$[b]	$S^* - S$ (Keyes)[c]
273.2	4.6	...	*0.008*[d]	0.006
363.2	525.9	0.090	.077	.097
373.2	760.0	.112	.096	.121
403.2	2026.0	.207	*.188*[d]	.216

[a] S^* from data of ref. 8; S from data of ref. 1. [b] Computed with the aid of eqs. (1) and (3). [c] Computed from data of Table V, ref. 2; see footnote 14. [d] Beyond the range of temperature and pressure of the experiments.

Tests for Consistency with other Thermal Data.—An indication of the consistency of the present vapor heat capacity results with other thermal data for water may also be obtained with the aid of eqs. (1) and (3). Values of the entropy of gas imperfection, $S^* - S$, were calculated from eqs. (1) and (3) and are tabulated with the "observed" results in Table III. Here, S^* and S represent the entropy at saturation pressure of ideal and real vapor, respectively. Values of $S^* - S$ computed from Keyes' equation of state are also included in Table III. The figures for $(S^* - S)_{obsd.}$ were obtained from the entropy and vapor pressure data given by Osborne,[1] *et al.*, and the values for S° and $\Delta S^\circ_{298.16}$ (liq. → gas) reported by Wagman, *et al.*[8] In this case the effect of gas imperfection is represented by both equations of state to within 0.05% of S°, although the differences in the calculated quantity, $S^* - S$, are about 15–20%. Analogous results were obtained in a similar comparison for the enthalpy of gas imperfection, which, like $S^* - S$, is related to $(\partial V/\partial T)_P$.

TABLE IV

THE SECOND AND THIRD VIRIAL COEFFICIENTS FOR WATER

T, °K.	V_g,[a] cc. mole^{-1}	B[b], cc. mole^{-1}	C[b], cc.^{2}mole^{-2}	$B + CP/RT$,[b] cc. mole^{-1}	$V_g - RT/P$,[a] cc. mole^{-1}
273.2	3,716,500	*−2070*	*−19.5* × 10^{5}	*−2080*	−2110
293.2	1,042,000	*−1310*	*−10.8*	*−1320*	−1090
313.2	352,140	− *930*	− *5.57*	− *945*	− 910
333.2	138,320	− *720*	− *2.26*	− *735*	− 740
343.2	90,896	− 651	− 1.056	− 662	− 667
353.2	61,404	− 597	− 0.060	− 598	− 598
363.2	42,534	− 555	+ 0.770	− 537	− 534
373.2	30,141	− 522	1.462	− 474	− 480
383.2	21,801	− *493*	*2.047*	− *403*	− 436

[a] From Table II, ref. 1; at saturation pressure. [b] Calculated from eq. (3); italicized numbers are for conditions outside the range of temperature or pressure of the experiments.

Table IV shows a comparison of the quantity, $B + CP/RT$, calculated from eqs. (1) and (3), with the equivalent quantity, $V_g - RT/P$, derived from the data of Osborne, *et al.*[1] The deviations of the volume imperfections given in Table IV are less than 0.02% of the experimental molal volumes in the temperature range 0 to 100°.

BARTLESVILLE, OKLAHOMA

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(15) F. G. Keyes, *J. Chem. Phys.*, **17**, 923 (1949).