trapped hydrogen atoms are detrapped clearly demonstrates what happens if hydrogen atoms are mobilized in the matrices. The reactions of mobile hydrogen atoms in such solid phases must be diffusion controlled especially at low temperature as is suggested from the suppression of hydrogen atom migration below 77 K and immobilization at 4.2 K. It is likely that the reactions would be more or less diffusion controlled even at 77 K, so that simple competition may not be assumed even for mobile hydrogen atoms. The steric and orientational factors may be also important for the diffusion-controlled reactions of hydrogen atoms in such solid phases.[9]

It is suggested that factors such as the efficiency of the hydrogen atom immobilization and the diffusion of hydrogen atoms in the matrices, as well as steric and orientational factors and the reactivities of hydrogen atoms with matrix and solute molecules are correlated in a complicated manner and play an important role in the selective formation of solute radicals at 77 K and its suppression at temperatures lower than 77 K. Unless all of these factors are properly taken into consideration, the sound understanding of the solid state reactions of hydrogen atoms may not be obtained.

Note Added in Proof. Recently Katsumura et al.[10] have reported that selective radical formation is not observed in the plastic crystal phase of neopentane. In the light of the present study, it may be suggested that the higher diffusion velocity of hydrogen atoms in the plastic crystal phase leads to a higher probability of recombination reaction 8 than that of abstraction reaction from solutes (reaction 7). They have also reported that the solute radical yield relative to the total yield in the crystal phase levels off at high irradiation doses. This may be also interpreted by the relative importance of recombination reaction 8 at higher doses. These results seem to suggest that the reactions of hydrogen atoms in crystalline neopentane are diffusion controlled.

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Thermodynamics of Electrolytes. 12. Dielectric Properties of Water and Debye–Hückel Parameters to 350 °C and 1 kbar

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In preparation for work with aqueous electrolytes at above saturation pressures and at temperatures to 350 °C, an equation was developed for the representation of the dielectric constant of water over this range. With this equation and an equation of state for water, the Debye–Hückel limiting law parameters for osmotic and activity coefficients, enthalpies, heat capacities, volumes, compressibilities, and expansibilities were calculated and are presented.

We are extending our investigations of the thermodynamic properties of aqueous electrolytes at high temperatures to conditions at higher-than-saturation pressure. It is expected that at these higher pressures the solutions will retain to higher temperatures the properties associated with strong electrolytes. As the critical temperature is approached along the saturation curve, the dielectric constant decreases rapidly and various properties can be expected to show anomalies. However at somewhat higher pressures, properties show more gradual change and should be subject to more accurate interpretation. Also many cases of practical interest, such as equilibria with solid phases under geological conditions, occur at above saturation pressure.

In earlier work focused on the saturation pressure, Silvester and Pitzer[1] developed an equation for the dielectric constant of water extending to 300 °C. While this equation included terms for pressure or density dependence, the pressure derivative of the dielectric constant is not as accurately represented as is desirable or possible. Consequently we sought a new form of equation which will more naturally represent the volume or pressure dependence of the dielectric constant while still representing its temperature dependence.

Dielectric Constant

The dielectric constant of water has been measured as function of temperature and pressure by relatively few investigators.[2-6] At temperatures above 70 °C there are only two sets of data, those of Akerlof and Oshry[5] along the vapor saturation curve from 100 to 370 °C and those of Heger[3] from 100 to 550 °C and saturation pressure to 5000 bar. The accuracy of most of the high temperature data is better than 1%. Below 70 °C, however, the data

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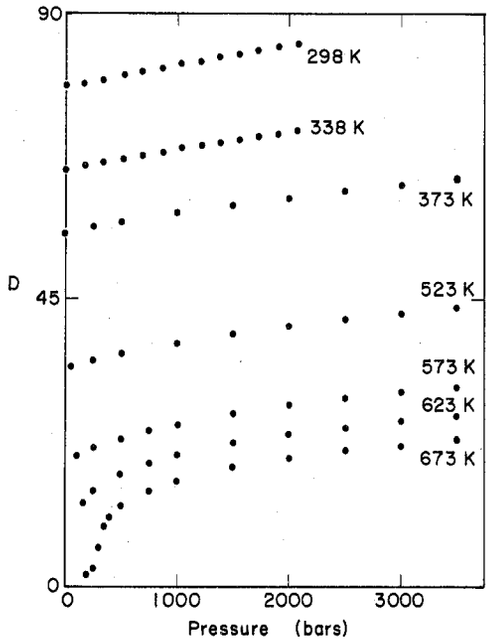

Figure 1. Values of the dielectric constant of water as a function of pressure at various temperatures. Note the logarithmic behavior at high temperature. The data at 338 and 298 K are from Dunn and Stokes;[6] all of the other values are from Heger.[3]

TABLE I: Values of the Constants in Eq 2-4 for the Dielectric Constant of Water

U_1 = 3.4279E2	U_6 = −1.8289E2
U_2 = −5.0866E-3	U_7 = −8.0325E3
U_3 = 9.4690E-7	U_8 = 4.2142E6
U_4 = −2.0525	U_9 = 2.1417
U_5 = 3.1159E3	

appear to have a much greater accuracy. Where direct comparison can be made the difference between Owen et al.,[2] Srinivasan and Kay,[4] and Dunn and Stokes[6] is approximately 0.1%. Because of the large differences in the accuracy between the low and high temperature data the low temperature data were fit preferentially. To accomplish this the high temperature data were weighted in such a way that the quality of the low temperature fit was not degraded.

In deciding the form of the equation used to fit the data, special attention was paid to the pressure dependence. Figure 1 shows that the dielectric constant is essentially linear with pressure at low temperatures but the dependence becomes logarithmic as the temperature is increased. An equation with this type of behavior was suggested by Tait in 1880 for volumetric data. In terms of the dielectric constant the equation takes the following form:

$$D = D_{1000} + C \ln\left(\frac{B + P}{B + 1000}\right) \quad (1)$$

D_{1000}, C, and B are temperature dependent parameters. The choice of 1000 bar for the reference (D_{1000}) was purely a matter of convenience; another pressure accessible at all temperatures could have been used. The expressions of temperature dependence for the three parameters are as follows:

$$D_{1000} = U_1 \exp[U_2T + U_3T^2] \quad (2)$$

$$C = U_4 + U_5/(U_6 + T) \quad (3)$$

$$B = U_7 + U_8/T + U_9T \quad (4)$$

The equation is valid in region of 0–350 °C and to 2000 bar below 70 °C and 5000 bar above 70 °C. The values

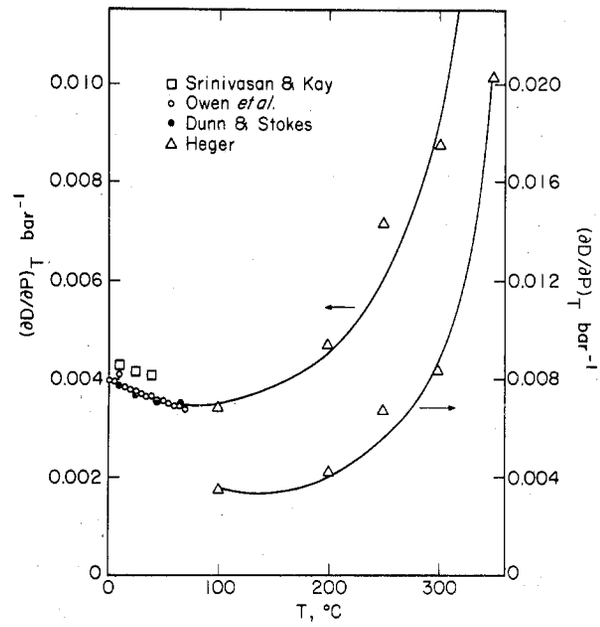

Figure 2. Values of $(\partial D/\partial P)_T = C/(B + P)$ along the vapor–liquid saturation curve. The points were determined from data at a single temperature; the curve is given by the equation fitted to all of the data. The right-hand curve goes with the right-hand scale and the left with the left. See comments to Figure 3.

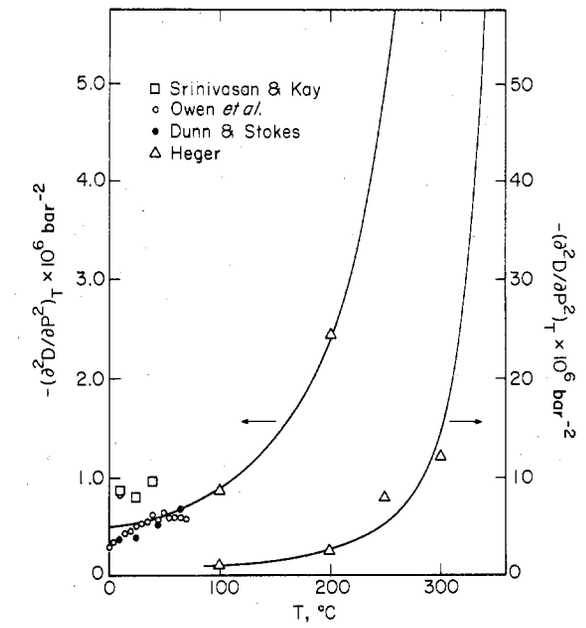

Figure 3. Values of $-(V^2D/\partial P^2)_T = C/(B + P)^2$ along the saturation curve; points and curve were determined as in Figure 2. Note that the detailed trend with temperature from the data of Owen et al.[2] is contrary to the general pattern of data at higher temperature. The right-hand curve goes with the right-hand scale and the left with the left.

of U_1–U_9 can be found in Table I. The temperature T and the pressure P are in units of Kelvin and bar, respectively. All of the data below 70 °C have been fit to better than 0.1%, however, the 25 °C data of Srinivasan and Kay[4] were deleted from the final fit as their slope did not agree with that obtained from the data of Owen et al.[2] and of Dunn and Stokes.[6] For the high temperature region only Heger's results were used. The data of Akerloff and Oshry[5] were deleted because the results were limited to pressures and temperatures along the saturation curve. The average residual in the high temperature data is approximately 0.2 but larger values appear at 100 °C and high pressures. The largest residual is 0.64 at 100 °C and 5000 bar. The poor fit at 100 °C indicates that the data

TABLE II. DEBYE-HUCKEL SLOPES FOR THE OSMOTIC COEFFICIENT, APHI

TEMP/C	PRESSURE/BARS						
	SAT	100	200	400	600	800	1000
0.	3.77E-01	3.75E-01	3.73E-01	3.70E-01	3.67E-01	3.64E-01	3.61E-01
10.	3.82E-01	3.80E-01	3.79E-01	3.75E-01	3.72E-01	3.69E-01	3.66E-01
20.	3.88E-01	3.86E-01	3.85E-01	3.81E-01	3.78E-01	3.75E-01	3.72E-01
25.	3.91E-01	3.90E-01	3.88E-01	3.84E-01	3.81E-01	3.78E-01	3.74E-01
30.	3.95E-01	3.93E-01	3.91E-01	3.87E-01	3.84E-01	3.81E-01	3.77E-01
40.	4.02E-01	4.00E-01	3.98E-01	3.94E-01	3.91E-01	3.87E-01	3.84E-01
50.	4.10E-01	4.08E-01	4.06E-01	4.02E-01	3.98E-01	3.94E-01	3.91E-01
60.	4.19E-01	4.17E-01	4.14E-01	4.10E-01	4.06E-01	4.02E-01	3.98E-01
70.	4.28E-01	4.26E-01	4.23E-01	4.19E-01	4.14E-01	4.10E-01	4.06E-01
80.	4.38E-01	4.36E-01	4.33E-01	4.28E-01	4.23E-01	4.19E-01	4.15E-01
90.	4.49E-01	4.46E-01	4.43E-01	4.38E-01	4.33E-01	4.28E-01	4.24E-01
100.	4.61E-01	4.57E-01	4.54E-01	4.48E-01	4.43E-01	4.38E-01	4.33E-01
110.	4.73E-01	4.69E-01	4.66E-01	4.60E-01	4.54E-01	4.48E-01	4.43E-01
120.	4.86E-01	4.82E-01	4.78E-01	4.71E-01	4.65E-01	4.59E-01	4.53E-01
130.	4.99E-01	4.95E-01	4.91E-01	4.84E-01	4.77E-01	4.70E-01	4.64E-01
140.	5.14E-01	5.10E-01	5.05E-01	4.97E-01	4.89E-01	4.82E-01	4.76E-01
150.	5.30E-01	5.25E-01	5.20E-01	5.11E-01	5.02E-01	4.95E-01	4.88E-01
160.	5.46E-01	5.41E-01	5.35E-01	5.25E-01	5.16E-01	5.08E-01	5.00E-01
170.	5.63E-01	5.58E-01	5.51E-01	5.40E-01	5.30E-01	5.21E-01	5.13E-01
180.	5.82E-01	5.76E-01	5.69E-01	5.56E-01	5.45E-01	5.35E-01	5.26E-01
190.	6.02E-01	5.95E-01	5.87E-01	5.73E-01	5.61E-01	5.50E-01	5.40E-01
200.	6.23E-01	6.15E-01	6.06E-01	5.91E-01	5.77E-01	5.65E-01	5.54E-01
210.	6.45E-01	6.37E-01	6.27E-01	6.10E-01	5.94E-01	5.81E-01	5.69E-01
220.	6.69E-01	6.60E-01	6.49E-01	6.29E-01	6.12E-01	5.98E-01	5.85E-01
230.	6.95E-01	6.85E-01	6.72E-01	6.50E-01	6.31E-01	6.15E-01	6.01E-01
240.	7.23E-01	7.13E-01	6.98E-01	6.72E-01	6.51E-01	6.33E-01	6.17E-01
250.	7.54E-01	7.42E-01	7.25E-01	6.95E-01	6.71E-01	6.51E-01	6.34E-01
260.	7.87E-01	7.75E-01	7.54E-01	7.20E-01	6.93E-01	6.70E-01	6.51E-01
270.	8.23E-01	8.11E-01	7.87E-01	7.47E-01	7.16E-01	6.90E-01	6.69E-01
280.	8.63E-01	8.51E-01	8.22E-01	7.76E-01	7.40E-01	7.11E-01	6.88E-01
290.	9.08E-01	8.98E-01	8.62E-01	8.06E-01	7.65E-01	7.33E-01	7.07E-01
300.	9.60E-01	9.52E-01	9.07E-01	8.40E-01	7.92E-01	7.55E-01	7.26E-01
310.	1.02E+00		9.60E-01	8.77E-01	8.20E-01	7.79E-01	7.46E-01
320.	1.09E+00		1.02E+00	9.19E-01	8.51E-01	8.03E-01	7.66E-01
330.	1.18E+00		1.10E+00	9.66E-01	8.84E-01	8.28E-01	7.87E-01
340.	1.29E+00		1.21E+00	1.02E+00	9.20E-01	8.55E-01	8.08E-01
350.	1.44E+00		1.36E+00	1.09E+00	9.60E-01	8.83E-01	8.30E-01

of Owen et al. and of Heger do not flow smoothly into one another. That this is true can be seen in Figures 2 and 3 where values of the first and second derivatives of D with pressure, obtained from fitting eq 1 to data at a single temperature, are plotted as functions of temperature. Owen's data indicate that $-(\partial^2 D/\partial P^2)_T$ should decrease above 70 °C whereas other data show that it increases markedly. Until more measurements can be made at temperatures above 70 °C this twist in data cannot be removed. The need for new data is also critical in the region above 250 °C where the derivatives of D change drastically.

Debye-Hückel Limiting Law Parameters

In the previous papers of this series we have defined Debye–Hückel parameters for enthalpy, heat capacity, and volume in a manner to make the coefficient unity for a 1:1 electrolyte for the partial molal function for the solute. With the use of analytical equations instead of graphical methods for most calculations, one seldom uses these partial molal enthalpies, etc., for the solute. That is not the quantity measured. Rather one measures total enthalpies, heat capacities, and volumes and these are simply related to apparent molal (rather than partial molal) quantities. Once one has used these apparent molal quantities in fitting the temperature and pressure dependency of the parameters in a general set of equations, the activity coefficient may be calculated directly at any temperature within the range of validity of the equations. There is no longer any need to obtain the partial molal enthalpy to obtain the temperature derivative of the activity coefficient (as there was when one made such calculations by graphical methods). In view of this shift of emphasis it seems best to redefine the Debye–Hückel parameters for enthalpy and heat capacity to yield a unit numerical coefficient for 1:1 electrolytes for the apparent molal function. The net result is a D–H parameter 2/3 as large as before. Redlich[7] and others have defined the Debye–Hückel parameter for volume in the manner we now advocate so no change is needed in that case. Although it may lead to some confusion, we retain the symbols A_H, A_J, A_V, etc. for these parameters in view of the wide usage of A_γ and A_ϕ for the parameters for activity and osmotic coefficients, respectively.

Debye–Hückel parameters for thermodynamic properties in aqueous solutions can be obtained solely from the volumetric and electrostatic properties of water. The volumetric properties for water were obtained from the Keenan–Keyes[8] equation of state and are valid to 1 kbar.

The equations for Debye–Hückel parameters for the various apparent molal quantities are defined as follows:

osmotic coefficient

$$A_\phi = \frac{1}{3}\left(\frac{2\pi N_0 \rho_w}{1000}\right)^{1/2}\left(\frac{e^2}{DkT}\right)^{3/2}$$

activity coefficient

$$A_\gamma = 3A_\phi$$

apparent molal enthalpy

$$A_H/RT = -6A_\phi\left[1 + T\left(\frac{\partial \ln D}{\partial T}\right)_P + \frac{T\alpha_w}{3}\right]$$

apparent molal heat capacity

$$A_J/R = [\partial(A_H/R)/\partial T]_P$$

apparent molal volume

$$A_V = -2A_\phi RT\left[3\left(\frac{\partial \ln D}{\partial P}\right)_T + \beta_w\right]$$

apparent molal isothermal compressibility

$$A_\kappa = (\partial A_V/\partial P)_T$$

apparent molal isobaric expansibility

$$A_{Ex} = (\partial A_H/\partial P)_T = (\partial A_V/\partial T)_P$$

where α_w is the coefficient of expansion and β_w the compressibility of water.

TABLE III. DEBYE-HUCKEL SLOPES FOR THE APPARENT MOLAL ENTHALPY, AH/RT

TEMP/C	PRESSURE/BARS						
	SAT	100	200	400	600	800	1000
0.	5.51E-01	5.44E-01	5.37E-01	5.21E-01	5.08E-01	4.98E-01	4.92E-01
10.	6.50E-01	6.41E-01	6.31E-01	6.14E-01	5.99E-01	5.87E-01	5.79E-01
20.	7.50E-01	7.39E-01	7.28E-01	7.07E-01	6.90E-01	6.75E-01	6.63E-01
25.	8.02E-01	7.89E-01	7.77E-01	7.55E-01	7.36E-01	7.20E-01	7.06E-01
30.	8.54E-01	8.41E-01	8.28E-01	8.04E-01	7.83E-01	7.65E-01	7.49E-01
40.	9.64E-01	9.48E-01	9.33E-01	9.05E-01	8.80E-01	8.58E-01	8.38E-01
50.	1.08E+00	1.06E+00	1.04E+00	1.01E+00	9.81E-01	9.54E-01	9.30E-01
60.	1.20E+00	1.18E+00	1.16E+00	1.12E+00	1.09E+00	1.05E+00	1.03E+00
70.	1.33E+00	1.30E+00	1.28E+00	1.24E+00	1.20E+00	1.16E+00	1.13E+00
80.	1.47E+00	1.44E+00	1.41E+00	1.36E+00	1.31E+00	1.27E+00	1.23E+00
90.	1.61E+00	1.58E+00	1.54E+00	1.48E+00	1.43E+00	1.38E+00	1.33E+00
100.	1.76E+00	1.72E+00	1.69E+00	1.61E+00	1.55E+00	1.50E+00	1.44E+00
110.	1.93E+00	1.88E+00	1.84E+00	1.75E+00	1.68E+00	1.62E+00	1.56E+00
120.	2.10E+00	2.05E+00	1.99E+00	1.90E+00	1.82E+00	1.74E+00	1.68E+00
130.	2.29E+00	2.23E+00	2.16E+00	2.05E+00	1.96E+00	1.87E+00	1.80E+00
140.	2.49E+00	2.42E+00	2.34E+00	2.22E+00	2.10E+00	2.01E+00	1.92E+00
150.	2.71E+00	2.62E+00	2.54E+00	2.39E+00	2.26E+00	2.15E+00	2.05E+00
160.	2.95E+00	2.85E+00	2.75E+00	2.57E+00	2.42E+00	2.30E+00	2.19E+00
170.	3.21E+00	3.09E+00	2.97E+00	2.77E+00	2.59E+00	2.45E+00	2.32E+00
180.	3.50E+00	3.36E+00	3.22E+00	2.98E+00	2.78E+00	2.61E+00	2.47E+00
190.	3.82E+00	3.66E+00	3.49E+00	3.20E+00	2.97E+00	2.78E+00	2.61E+00
200.	4.18E+00	3.99E+00	3.78E+00	3.44E+00	3.17E+00	2.95E+00	2.77E+00
210.	4.58E+00	4.36E+00	4.11E+00	3.71E+00	3.39E+00	3.13E+00	2.93E+00
220.	5.04E+00	4.78E+00	4.48E+00	4.00E+00	3.62E+00	3.33E+00	3.09E+00
230.	5.56E+00	5.26E+00	4.89E+00	4.31E+00	3.87E+00	3.53E+00	3.25E+00
240.	6.17E+00	5.82E+00	5.37E+00	4.66E+00	4.13E+00	3.74E+00	3.42E+00
250.	6.89E+00	6.49E+00	5.92E+00	5.05E+00	4.42E+00	3.96E+00	3.60E+00
260.	7.75E+00	7.30E+00	6.57E+00	5.48E+00	4.73E+00	4.19E+00	3.78E+00
270.	8.81E+00	8.30E+00	7.35E+00	5.98E+00	5.07E+00	4.43E+00	3.96E+00
280.	1.01E+01	9.58E+00	8.31E+00	6.56E+00	5.45E+00	4.68E+00	4.14E+00
290.	1.18E+01	1.13E+01	9.54E+00	7.25E+00	5.86E+00	4.95E+00	4.32E+00
300.	1.40E+01	1.36E+01	1.12E+01	8.08E+00	6.34E+00	5.24E+00	4.51E+00
310.	1.71E+01		1.34E+01	9.12E+00	6.88E+00	5.55E+00	4.69E+00
320.	2.14E+01		1.66E+01	1.05E+01	7.52E+00	5.88E+00	4.87E+00
330.	2.80E+01		2.16E+01	1.22E+01	8.29E+00	6.25E+00	5.05E+00
340.	3.86E+01		3.03E+01	1.48E+01	9.25E+00	6.66E+00	5.22E+00
350.	5.73E+01		4.74E+01	1.86E+01	1.05E+01	7.13E+00	5.39E+00

TABLE IV. DEBYE-HUCKEL SLOPES FOR THE APPARENT MOLAL VOLUME, AV/(CC/MOLE)

TEMP/C	PRESSURE/BARS						
	SAT	100	200	400	600	800	1000
0.	1.51E+00	1.48E+00	1.46E+00	1.41E+00	1.37E+00	1.34E+00	1.31E+00
10.	1.63E+00	1.61E+00	1.58E+00	1.53E+00	1.48E+00	1.43E+00	1.38E+00
20.	1.78E+00	1.75E+00	1.72E+00	1.66E+00	1.59E+00	1.53E+00	1.47E+00
25.	1.87E+00	1.83E+00	1.80E+00	1.73E+00	1.66E+00	1.59E+00	1.52E+00
30.	1.96E+00	1.92E+00	1.88E+00	1.80E+00	1.72E+00	1.65E+00	1.57E+00
40.	2.15E+00	2.10E+00	2.06E+00	1.96E+00	1.87E+00	1.78E+00	1.69E+00
50.	2.37E+00	2.31E+00	2.26E+00	2.15E+00	2.04E+00	1.93E+00	1.83E+00
60.	2.62E+00	2.55E+00	2.49E+00	2.36E+00	2.23E+00	2.11E+00	2.00E+00
70.	2.91E+00	2.83E+00	2.75E+00	2.59E+00	2.45E+00	2.31E+00	2.18E+00
80.	3.23E+00	3.14E+00	3.04E+00	2.86E+00	2.69E+00	2.53E+00	2.39E+00
90.	3.61E+00	3.49E+00	3.38E+00	3.17E+00	2.97E+00	2.79E+00	2.62E+00
100.	4.04E+00	3.90E+00	3.77E+00	3.52E+00	3.28E+00	3.07E+00	2.88E+00
110.	4.53E+00	4.37E+00	4.21E+00	3.91E+00	3.64E+00	3.40E+00	3.17E+00
120.	5.11E+00	4.91E+00	4.72E+00	4.36E+00	4.04E+00	3.76E+00	3.50E+00
130.	5.77E+00	5.53E+00	5.30E+00	4.88E+00	4.50E+00	4.17E+00	3.87E+00
140.	6.54E+00	6.26E+00	5.98E+00	5.47E+00	5.02E+00	4.63E+00	4.28E+00
150.	7.44E+00	7.10E+00	6.76E+00	6.15E+00	5.61E+00	5.15E+00	4.74E+00
160.	8.49E+00	8.08E+00	7.66E+00	6.92E+00	6.28E+00	5.73E+00	5.26E+00
170.	9.73E+00	9.23E+00	8.72E+00	7.81E+00	7.05E+00	6.40E+00	5.84E+00
180.	1.12E+01	1.06E+01	9.95E+00	8.85E+00	7.92E+00	7.15E+00	6.49E+00
190.	1.29E+01	1.22E+01	1.14E+01	1.00E+01	8.92E+00	7.99E+00	7.22E+00
200.	1.50E+01	1.41E+01	1.31E+01	1.14E+01	1.01E+01	8.96E+00	8.04E+00
210.	1.75E+01	1.64E+01	1.51E+01	1.30E+01	1.14E+01	1.01E+01	8.96E+00
220.	2.05E+01	1.91E+01	1.76E+01	1.49E+01	1.29E+01	1.13E+01	9.99E+00
230.	2.41E+01	2.25E+01	2.05E+01	1.72E+01	1.47E+01	1.27E+01	1.12E+01
240.	2.86E+01	2.66E+01	2.40E+01	1.98E+01	1.67E+01	1.43E+01	1.25E+01
250.	3.42E+01	3.18E+01	2.84E+01	2.30E+01	1.91E+01	1.62E+01	1.39E+01
260.	4.12E+01	3.84E+01	3.38E+01	2.69E+01	2.19E+01	1.83E+01	1.56E+01
270.	5.02E+01	4.70E+01	4.07E+01	3.15E+01	2.52E+01	2.08E+01	1.75E+01
280.	6.18E+01	5.82E+01	4.96E+01	3.72E+01	2.92E+01	2.36E+01	1.97E+01
290.	7.72E+01	7.36E+01	6.13E+01	4.44E+01	3.39E+01	2.70E+01	2.21E+01
300.	9.80E+01	9.51E+01	7.71E+01	5.35E+01	3.96E+01	3.08E+01	2.49E+01
310.	1.27E+02		9.93E+01	6.52E+01	4.66E+01	3.54E+01	2.81E+01
320.	1.69E+02		1.32E+02	8.09E+01	5.53E+01	4.08E+01	3.17E+01
330.	2.31E+02		1.83E+02	1.02E+02	6.63E+01	4.73E+01	3.59E+01
340.	3.30E+02		2.71E+02	1.33E+02	8.05E+01	5.51E+01	4.08E+01
350.	4.93E+02		4.38E+02	1.79E+02	9.92E+01	6.47E+01	4.65E+01

As can be seen from plots of the parameters A_ϕ and A_H along the saturation curve, Figures 4 and 5, both become exponential as the temperature approaches the critical point of water, 374 °C. The large curvature for the parameters becomes a problem above 300 °C. The spacing of data points is 50 ° and therefore the values of the second derivatives at temperatures above 300 °C become very sensitive to small errors in the data. The same can be said about the pressure derivative above 300 °C.

The calculations show that all of the parameters are monotonic functions of temperature except A_κ, which goes through a minimum between 345 and 350 °C at saturation pressure. A_κ is well behaved at pressures greater than the saturation pressure, and the pressure derivatives of the dielectric constant evaluated using only data at 350 °C agree within 2% of the values obtained from the overall

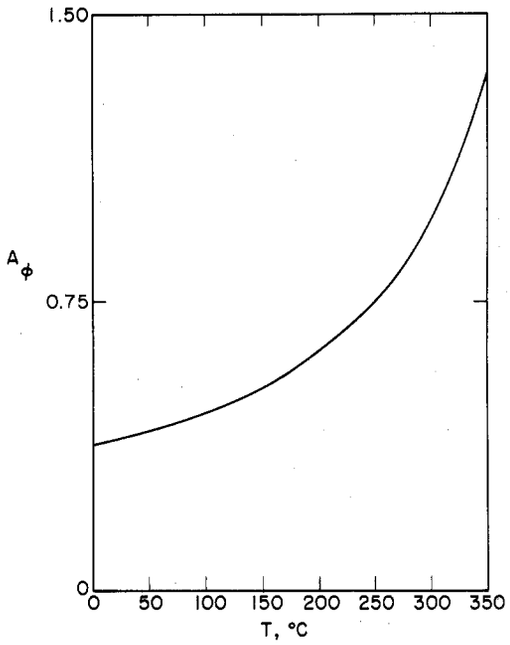

Figure 4. A_ϕ (osmotic coefficient) as a function of temperature along the vapor saturation curve.

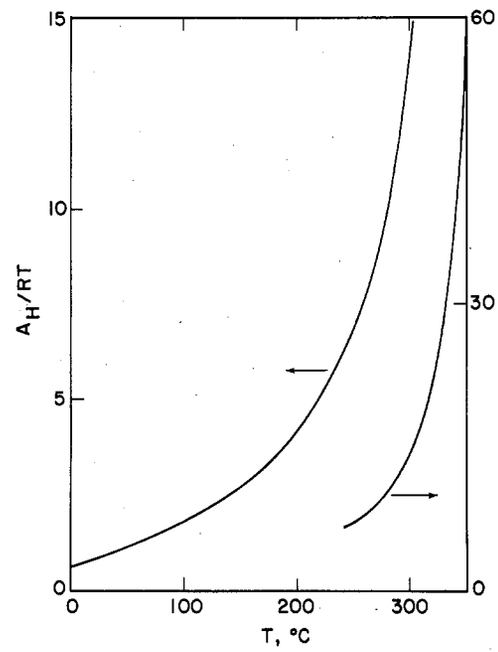

Figure 5. A_H/RT (apparent molal enthalpy) as a function of temperature along the vapor saturation curve. The right-hand curve goes with the right-hand scale and the left with the left.

fit, indicating that the minimum may be real.

The values A_V from 0 to 70 °C have been compared to those calculated by Redlich and Meyer[7] and were found to agree to within 1% from 10 to 50 °C and within 5% over the entire range. The disagreement at temperatures above 50 °C is the result of our effort to match the low and high temperature dielectric data. However, as has been noted above, the data of Owen et al. do not extrapolate smoothly into the data at and above 100 °C and therefore derivatives calculated solely from their data may be inaccurate. The overall accuracy of the parameters is very difficult to assign; however, from the numerous fits that were tried in this effort and the results of Silvester and Pitzer,[1] it is felt that the errors for A_ϕ, A_H, and A_V are less than 5% and the error for A_J, A_κ, A_{Ex} less than 10% at temperatures below 300 °C. Above 300 °C near the saturation pressure the error probably increases appreciably and may be as much as 25% at 350 °C.

Helgeson and Kirkham[9] have also presented an equation for the dielectric constant of water which was designed to fit over a considerably wider range of temperature and pressure. Thus it is not surprising that their equation does not fit as well over the more limited range that we consider.

Values for the Debye–Hückel parameters at various temperatures and pressures are given in Tables II–VII.

These Debye–Hückel parameters will be needed in developing an understanding of electrolyte solutions at advanced temperatures. There are various indications that the special structural aspects of water diminish above 50 °C. In the high-temperature domain water presumably becomes a more "normal" polar liquid and detailed theoretical treatment may become less difficult.

For the Debye–Hückel or equivalent treatments of electrolytes one needs the dielectric properties next to the ions. If the special structural aspects are less important, a dipole model for the solvent may be more adequate. However, the linearization approximations based on the smallness of e^2/DkT is actually poorer at high temperature since D decreases faster than T increases. If the ion–solvent interactions can be better understood in detail, then it should be possible to give a molecular-level interpretation to the virial coefficients that represent short-range interionic interactions.

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Supplementary Material Available: Values of the Debye–Hückel parameters for the apparent molal heat capacity, expansibility, and compressibility are presented in Tables V, VI, and VII (3 pages). Ordering information is available on any current masthead page.

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