

# Thermodynamics of Concentrated Electrolyte Mixtures. 4. Pitzer-Debye-Hückel Limiting Slopes for Water from 0 to 100 °C and from 1 atm to 1 kbar

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The recently developed Pitzer formalism has provided a very valuable tool for the analysis and prediction of the thermodynamic properties of concentrated electrolytes. The formalism is clearly applicable to the analysis of pressure and temperature effects. However, minor discrepancies in the definitions of limiting slopes and some major discrepancies in the numerical evaluations of these slopes have led to some confusion. In this paper we summarize the most useful definitions of the limiting slopes for osmotic coefficients, activity coefficients, enthalpies, heat capacities, volumes, expansibilities, and compressibilities. We then present numerical values for these slopes to five significant figures in the ranges 0–100 °C and 1 atm–1 kbar. We also compared some of the recent equations for the dielectric constant of water over wide temperature and pressure ranges.

## Introduction

During the past few years Pitzer and co-workers (1–7) have developed a set of equations that describe the properties of electrolyte solutions not only at high concentrations but also at elevated temperatures and pressures. These equations are a form of Debye-Hückel theory extended with the specific interaction approach with empirical interaction coefficients. Thus, these equations inevitably have limiting law slopes ( $\beta$ ). This similarity between the limiting slopes of the Pitzer equations and the Debye-Hückel limiting slopes has led to some confusion about both the numerical values and the definitions of the slopes. For example, in their original work Pitzer and Mayorga (2) used a value of 0.391 at 25 °C and 1-atm pressure for  $A_\phi$ , the limiting slope of the osmotic coefficient equation. However, the values of 0.392, 0.3921, and 0.39211 were used by Harvie and Wear (9), Ananthaswamy and Atkinson (10), and Roy et al. (11), respectively, in their works. Recently, Bradley and Pitzer (BP) (12) have published a value of 0.391 at saturation pressure. Also, Rogers, and Pitzer (13) list a value of 0.391 at saturation pressure. Also, Rogers and Pitzer (13) list a value of 0.391 at 25 °C and 1-atm pressure. However, Rogers and Pitzer (14) used a value of 0.3915 in their reinvestigation of  $\text{CaCl}_2$  solutions and mixtures at high concentrations. The difference, which is only about 0.25% for different values of  $A_\phi$ , may creep up to 50% when it comes to  $A_j$  (limiting slope for apparent molal heat capacity) and  $A_K$  (slope for apparent molal compressibility). Thus,  $A_j$  values used by Silvester and Pitzer (7), Bradley and Pitzer (12), Clarke and Glew (15), and Helgeson and Kirkham (HK) (16) are 12.8, 11.65, 9.211 and 13.22 cal kg<sup>1/2</sup> mol<sup>-3/2</sup> K<sup>-1</sup>, respectively. These variations are largely due to the use of different values for the dielectric constant and volume properties of water. Clarke and Glew (15) have opined that both the Silvester and Pitzer (7) and Bradley and Pitzer (12) values are erroneous because they are based

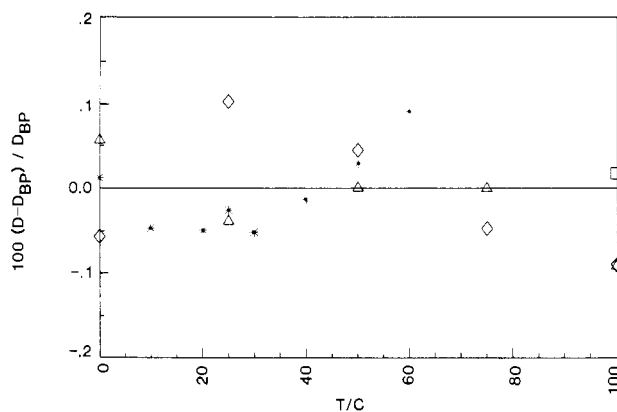


Figure 1. Percentage deviation of dielectric constants of water at 1-atm pressure from the corresponding values calculated by using the Bradley-Pitzer equation ( $D_{BP}$ ) vs. temperature: (\*) IUPAC, ( $\diamond$ ) UF equation, ( $\Delta$ ) KD equation, ( $\square$ ) HK equation.

on the same input data. In addition Bradley and Pitzer (12) and Rogers and Pitzer (14) have listed the slope values only up to three significant figures, which may discourage many workers from using these values since the dielectric properties for water are considered to be known up to four significant figures and the volume properties up to six significant figures.

The Pitzer formalism essentially consists of the virial expressions for the thermodynamic properties of the single-electrolyte solutions such as the excess Gibbs energy, osmotic coefficient, and activity coefficient in terms of the virial coefficients  $\beta^0$ ,  $\beta^1$ , and  $C^\phi$ . The Pitzer equation for the activity coefficient ( $\gamma_{MX}$ ) of a pure electrolyte in aqueous solution is of the form

$$\ln \gamma_{MX} = f(I) + \sum_X B_{MX} m_M m_X + \text{higher terms}$$

where  $f(I)$  is essentially a Debye-Hückel term depending only on ionic strength,  $B_{MX}$  is a virial coefficient representing the interaction of the M ion with the X ion, and  $m_M$  and  $m_X$  are the concentrations of the ions. A virtue of the Pitzer equations (1–4) is that the virial coefficients  $\beta^0$ ,  $\beta^1$ , and  $C^\phi$  obtained by studying the single-electrolyte solutions are useful in describing multicomponent solutions with the addition of  $\theta$  and  $\psi$  terms. These  $\theta$  and  $\psi$  terms can be calculated from the difference between the observed behavior of a mixed-electrolyte solution and the behavior predicted by an appropriate combination of the respective single-electrolyte equations. Thus, over a period of time, it is hoped that a full set of  $\beta^0$ ,  $\beta^1$ ,  $C^\phi$ ,  $\theta$ ,  $\psi$ , etc., coefficients can be tabulated so that the properties of any single-component or multicomponent electrolyte solution can be calculated over a wide range of concentration, temperature, and pressure by using these coefficients. This long-term goal appears to be in trouble because it is not possible to compare either the single-electrolyte parameter  $\beta^0$ ,  $\beta^1$ , and  $C^\phi$  or the mixing term  $\theta$  and  $\psi$  obtained by different workers unless they are all calculated by using the same values for the limiting

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Table I. Comparison of Limiting Slopd Definitions

slope	Pitzer	Helgeson and Kirkham	Redlich, Meyer, and Millero
$A_\phi$	$A_\phi = 1/3(2\pi N_0 d/1000)^{1/2} [e^2/(DkT)]^{3/2}$		
$A_\gamma$	$3A_\phi$	$3A_\phi/2.3026$	
$A_H$	$4RT^2(\partial A_\phi/\partial T)_P$	$6RT^2(\partial A_\phi/\partial T)_P$	$6RT^2(\partial A_\phi/\partial T)$
$A_J$	$\partial/\partial T(4RT^2\partial A_\phi/\partial T)_P$	$(\partial A_H/\partial T)_P = \partial/\partial T(6RT^2\partial A_\phi/\partial T)_P$	
$A_v$	$-4RT(\partial A_\phi/\partial P)_T$	$-6RT(\partial A_\phi/\partial P)_T$	$\partial/\partial T(6RT^2\partial A_\phi/\partial T)$
$A_E$	$(\partial A_v/\partial T)_P = (\partial A_H/\partial P)_T^a$	$-\partial/\partial T(6RT\partial A_\phi/\partial P)_T$	$S_v = -4RT(\partial A_\phi/\partial P)_T^b$
$A_K$	$(\partial A_v/\partial P)_T$	$-6RT(\partial^2 A_\phi/\partial P^2)_T$	$S_E = \partial S_v/\partial T - \alpha_\alpha(S_v/2)$ $S_K = -(\partial S_v/\partial P + \beta S_v/2)$

<sup>a</sup> Prof. Pitzer has indicated that “ $(\partial H/\partial P)_T$ ” is an error in the Bradley-Pitzer (12) paper and should be omitted so that  $A_E = (\partial A_v/\partial T)_P$  only. <sup>b</sup> Prof. Millero's  $S_v$ ,  $S_E$ , and  $S_K$  are to be used with molarity scale. However,  $S_E$  and  $S_K$  are different from  $A_E$  and  $A_K$  of Pitzer-Debye-Hückel slopes.

Table II. Pitzer Equations

$$\phi - 1 = -|Z_M Z_X| A_\phi \frac{I^{1/2}}{1 + bI^{1/2}} + 2 \left( \frac{\nu_M \nu_X}{\nu} \right) m B_{MX}^\phi + \frac{2(\nu_M \nu_X)^{3/2}}{\nu} m^2 C_{MX}^\phi$$

$$\ln \gamma_{MX} = -|Z_M Z_X| A_\phi \left[ \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right] + 2 \left( \frac{\nu_M \nu_X}{\nu} \right) m B_{MX}^\gamma + 3 \frac{(\nu_M \nu_X)^{3/2}}{\nu} m^2 C_{MX}^\phi$$

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} \exp(-x)$$

$$B_{MX}^\gamma = 2\beta_{MX}^{(0)} + \frac{2\beta_{MX}^{(1)}}{x^2} \left[ 1 - \left( 1 + x - \frac{x^2}{2} \right) \exp(-x) \right]$$

$$x = \alpha I^{1/2}$$

$$\phi_L = \nu |Z_M Z_X| A_H \frac{1}{2b} \ln(1 + bI^{1/2}) - 2(\nu_M \nu_X) RT^2 m B_{MX}^L - (\nu_M \nu_X)^{3/2} RT^2 m^2 C_{MX}^L$$

$$A_H = 4RT^2(\partial A_\phi/\partial T)_P$$

$$B_{MX}^L = \partial \beta_{MX}^{(0)}/\partial T + (\partial \beta_{MX}^{(1)}/\partial T)(2/x^2)[1 - (1 + x)e^{-x}]$$

$$C_{MX}^L = \partial C_{MX}^\phi/\partial T$$

$$\phi_{C_p} = \bar{C}_{p_2}^\circ + \nu |Z_M Z_X| A_J \frac{1}{2b} \ln(1 + bI^{1/2}) - 2(\nu_M \nu_X) RT^2 m B_{MX}^J - (\nu_M \nu_X)^{3/2} RT^2 m^2 C_{MX}^J$$

$$A_J = (\partial A_H/\partial T)_P$$

$$B_{MX}^J = \partial B_{MX}^L/\partial T + (2/T) B_{MX}^L$$

$$C_{MX}^J = \frac{\partial C_{MX}^L}{\partial T} + \frac{2}{T} C_{MX}^L = \frac{\partial^2 C_{MX}^\phi}{\partial T^2} + \frac{2}{T} \frac{\partial C_{MX}^\phi}{\partial T}$$

$$\phi_v = \phi_v^\circ + \nu |Z_M Z_X| (A_v/2b) \ln(1 + bI^{1/2}) + \nu RT(\nu_M \nu_X/\nu) m B_{MX}^v + RT(\nu_M \nu_X)^{3/2} m^2 C_{MX}^v$$

$$A_v = -4RT(\partial A_\phi/\partial P)_T$$

$$B_{MX}^v = \partial B_{MX}^\gamma/\partial P$$

$$= 2(\partial \beta_{MX}^{(0)}/\partial P) + 2(\partial \beta_{MX}^{(1)}/\partial P)(1/x^2)[1 - (1 + x - x^2/2)e^{-x}]$$

$$C_{MX}^v = \frac{\partial C_{MX}^\phi}{\partial P} - \frac{2}{3} \frac{\partial B_{MX}^\gamma}{\partial m}$$

$$\phi_E = \phi_E^\circ + \nu |Z_M Z_X| A_E (1/2b) \ln(1 + bI^{1/2}) + \nu RT(\nu_M \nu_X/\nu) m B_{MX}^E + (\nu_M \nu_X)^{3/2} RT m^2 C_{MX}^E$$

$$\phi_E^\circ = (\partial \phi_v^\circ/\partial T)_P$$

$$A_E = (\partial A_v/\partial T)_P$$

$$B_{MX}^E = \partial B_{MX}^v/\partial T$$

$$C_{MX}^E = \partial C_{MX}^v/\partial T$$

$$\phi_K = \phi_K^\circ - \nu |Z_M Z_X| A_K (1/2b) \ln(1 + bI^{1/2}) - \nu RT(\nu_M \nu_X/\nu) m B_{MX}^E - RT(\nu_M \nu_X)^{3/2} m^2 C_{MX}^E$$

$$\phi_K^\circ = -(\partial \phi_v^\circ/\partial P)_T$$

$$A_K = \partial A_v/\partial P$$

$$B_{MX}^E = \partial B_{MX}^v/\partial P$$

$$C_{MX}^E = \partial C_{MX}^v/\partial P$$

<sup>a</sup> In the equations listed,  $\alpha = 2.0$ ,  $b = 1.2$ , and  $I$  is the ionic strength (molality basis).

Table III. Pitzer-Debye-Hückel Limiting Slope Definitions<sup>a</sup>

$$A_\phi = 1/3(2\pi Nd/1000)^{1/2}[e^2/(DkT)]^{3/2}$$

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

$$A_H = 4RT^2(\partial A_\phi/\partial T)_P$$

$$= -6RT^2 A_\phi [1/T + \partial \ln D/\partial T + \alpha/3]$$

$$A_J = (\partial A_H/\partial T)_P$$

$$= 3A_\phi RT \left[ \frac{1}{T} + 2 \left( \frac{\partial \ln D}{\partial T} \right) + 5T \left( \frac{\partial \ln D}{\partial T} \right)^2 + \right.$$

$$\left. 2T \left( \frac{\partial \ln D}{\partial T} \right) \alpha + 2/3 \alpha + T \alpha^2 - \frac{2T}{D} \frac{\partial^2 D}{\partial T^2} - \frac{2T}{3V} \frac{\partial^2 V}{\partial T^2} \right]$$

$$A_v = -4RT(\partial A_\phi/\partial P)_T$$

$$= 6RTA_\phi \left( \frac{\partial \ln D}{\partial P} - \frac{\beta}{3} \right)$$

$$A_E = 6RTA_\phi \left[ \left( \frac{\partial \ln D}{\partial P} - \frac{\beta}{3} \right) \left\{ \frac{1}{T} - \frac{3}{2} \left( \frac{\partial \ln D}{\partial T} + \frac{\alpha}{3} \right) \right\} + \right.$$

$$\left. \frac{\partial^2 \ln D}{\partial T \partial P} - \frac{1}{3} \frac{\partial \beta}{\partial T} \right]$$

$$A_K = 6RTA_\phi \left[ \frac{\partial^2 \ln D}{\partial P^2} - \frac{1}{3} \frac{\partial \beta}{\partial P} - \frac{3}{2} \left( \frac{\partial \ln D}{\partial P} - \frac{\beta}{3} \right)^2 \right]$$

<sup>a</sup>  $\alpha = (1/V)(dV/dT)$  = coefficient of expansion of water;  $\beta = -(1/V)(dV/dP)$  = compressibility of water;  $D$  = dielectric constant of water;  $d$  = density of water;  $N$  = Avogadro number =  $6.022045 \times 10^{23}$ ;  $k$  = Boltzmann constant =  $1.38066 \times 10^{-16}$ ;  $e$  = charge of electron =  $4.803242 \times 10^{-10}$  esu;  $R$  =  $8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$ ; =  $83.1441 \text{ cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1}$ .

slopes. In addition, there is a difference in the current definitions of the limiting slopes that are used in the Pitzer equations and the conventional Debye-Hückel slopes. We suggest that the slopes in the Pitzer equations be called the "Pitzer-Debye-Hückel limiting slopes".

In this article we (i) compare some of the recent equations for the dielectric constant of water over wide temperature and pressure ranges, (ii) summarize the various definitions of the limiting slopes that are now in use, and (iii) list the values of the Pitzer-Debye-Hückel slopes in the range 0–100 °C and 1 atm–1 kbar.

### Dielectric Constant Equations

Recently Uematsu and Franck (UF) (17), Bradley and Pitzer (12), Helgeson and Kirkham (16), and Khodakovskiy and Dorofeyeva (KD) (18) have published equations for representing the dielectric constants of water over a broad range of temperatures and pressures. All these equations were obtained by a least-squares fitting of the available experimental data. The key sources of experimental data for these equations are the works of Heger (19), Akerlof and Oshry (20), Owen et al. (21), Malmberg and Maryott (22), Lees (23), Vidulich and Kay (24), Srinivasan and Kay (25), and Dunn and Stokes (26) although several other data sources were also considered in the least-squares fits on a lower weight basis.

Bradley and Pitzer (12) fitted the experimental dielectric constant data (19–21, 25, 26) to a form of the Tait equation which describes the dielectric constant of water in the range 0–350 °C and saturation pressure to 2000 bar below 70 °C and 5000 bar above 70 °C. Their equation is

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

where  $D_{1000}$ ,  $C$ , and  $B$  are temperature-dependent parameters and  $P$  is the pressure in bars. The Uematsu and Franck (UF) equation (17) represents the dielectric constant of water over the temperature range 0–550 °C and the pressure range up to 5 kbar. The Helgeson and Kirkham (HK) equation (16) rep-

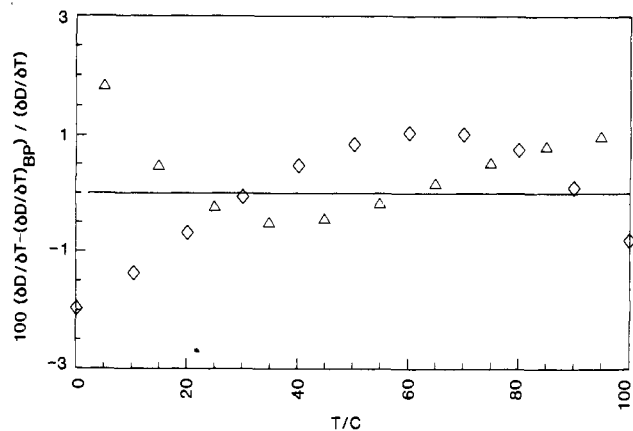


Figure 2. Percentage deviation of  $(\partial D/\partial T)_P$  values at 1-atm pressure from the corresponding values calculated by using the Bradley-Pitzer equation  $((\partial D/\partial T)_{BP})$  vs. temperature: ( $\Delta$ ) KD equation, ( $\diamond$ ) UF equation.

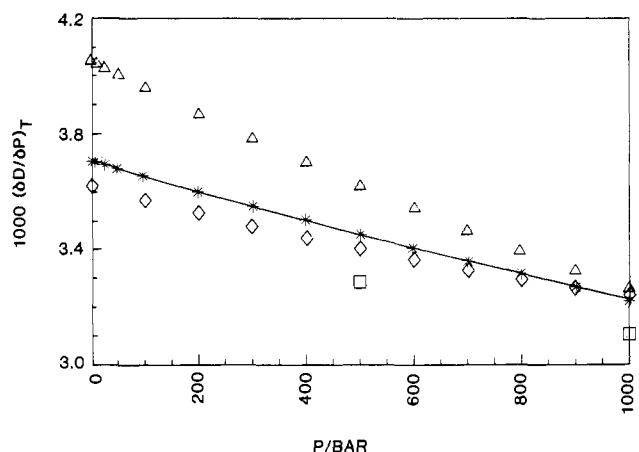


Figure 3. Plot of  $(\partial D/\partial P)_T$  at 25 °C vs. pressure: (\*) BP equation, ( $\Delta$ ) UF equation, ( $\diamond$ ) KD equation, ( $\square$ ) HK equation.

resents the dielectric constant of water in the temperature range 0–550 °C and pressures up to 5 kbar. The Khodakovskiy and Dorofeyeva (KD) equation (18) represents the dielectric constant of water over the temperature and pressure ranges 0–300 °C and 1–5 kbar.

The dielectric constants calculated from these four equations are shown the Figure 1, along with the values recommended by IUPAC (27). From Figure 1, it is evident that the Bradley and Pitzer (BP) equation (12) very closely reproduces the IUPAC data at 1-atm pressure. Also, the dielectric constant values calculated from the other three equations agree with the values calculated by using the BP equation to within about +0.1%. The deviations of  $(\partial D/\partial T)_P$  values at 1 atm, calculated by using the UF equation and the KD equation from the corresponding values calculated by using the BP equation  $((\partial D/\partial T)_{BP})$ , are shown in Figure 2. Figure 2 reveals that at 1-atm pressure over the temperature range 0–100 °C the  $(\partial D/\partial T)_P$  values calculated with the UF and KD equations are randomly scattered around the values from the BP equation with a maximum deviation of about  $\pm 2\%$ . The  $(\partial D/\partial P)_T$  values at 25 °C calculated with UF, BP, KD, and HK equations are shown in Figure 3. From this figure it is clear that  $(\partial D/\partial P)_T$  values from the BP equation are lower than the values calculated from the UF equation but higher than the values calculated by using the KD and HK equations. The  $(\partial D/\partial P)_T$  values at 25 °C over the pressure range 1 atm–1 kbar, calculated by using the BP equation ( $-5.5 \times 10^{-7}$  to  $-4.2 \times 10^{-7}$ ) are higher than the values obtained from the UF equation ( $-9.4 \times 10^{-7}$  to  $-6.3 \times$

Table IV. Pitzer-Debye-Hückel Slopes for the Osmotic Coefficients ( $A_\phi$ )<sup>a</sup>

temp/°C	press./bar						
	1 <sup>b</sup>	50	200	400	600	800	1000
0.0	0.376 72	0.375 91	0.373 47	0.370 30	0.367 22	0.364 22	0.361 31
5.0	0.379 33	0.378 51	0.376 01	0.372 77	0.369 64	0.366 60	0.363 65
10.0	0.382 11	0.381 27	0.378 71	0.375 40	0.372 21	0.369 12	0.366 12
15.0	0.385 06	0.384 19	0.381 57	0.378 19	0.374 93	0.371 78	0.368 74
20.0	0.388 17	0.387 29	0.384 59	0.381 13	0.377 79	0.374 58	0.371 49
25.0	0.391 45	0.390 53	0.387 77	0.384 22	0.380 81	0.377 53	0.374 38
30.0	0.394 89	0.393 94	0.391 10	0.387 46	0.383 97	0.380 62	0.377 40
35.0	0.398 49	0.397 52	0.394 60	0.390 85	0.387 27	0.383 84	0.380 55
40.0	0.402 26	0.401 26	0.398 25	0.394 39	0.390 71	0.387 20	0.383 83
45.0	0.406 20	0.405 16	0.402 05	0.398 08	0.394 30	0.390 69	0.387 24
50.0	0.410 29	0.409 22	0.406 01	0.401 92	0.398 03	0.394 32	0.390 77
55.0	0.414 56	0.413 45	0.410 13	0.405 91	0.401 89	0.398 07	0.394 43
60.0	0.418 99	0.417 84	0.414 40	0.410 04	0.405 90	0.401 97	0.398 22
65.0	0.423 58	0.422 39	0.418 83	0.414 32	0.410 04	0.405 99	0.402 14
70.0	0.428 34	0.427 11	0.423 42	0.418 74	0.414 33	0.410 14	0.406 18
75.0	0.433 28	0.431 99	0.428 16	0.423 32	0.418 75	0.414 43	0.410 34
80.0	0.438 38	0.437 04	0.433 07	0.428 04	0.423 31	0.418 84	0.414 62
85.0	0.443 66	0.442 27	0.438 13	0.432 91	0.428 01	0.423 39	0.419 03
90.0	0.449 11	0.447 66	0.443 36	0.437 93	0.432 85	0.428 07	0.423 56
95.0	0.454 75	0.453 23	0.448 75	0.443 11	0.437 83	0.432 88	0.428 22
100.0	0.460 56	0.458 98	0.454 30	0.448 43	0.442 95	0.437 82	0.432 99

<sup>a</sup>  $A_\phi$  is in  $\text{kg}^{1/2} \text{mol}^{-1/2}$ . <sup>b</sup> 1 atm.

Table V. Pitzer-Debye-Hückel Slopes for Apparent Molal Enthalpy ( $10^{-3}A_H$ )<sup>a</sup>

temp/°C	press./bar						
	1 <sup>b</sup>	50	200	400	600	800	1000
0.0	1.2573	1.2472	1.2192	1.1875	1.1615	1.1408	1.1250
5.0	1.3883	1.3776	1.3476	1.3127	1.2833	1.2589	1.2392
10.0	1.5269	1.5153	1.4825	1.4438	1.4105	1.3822	1.3583
15.0	1.6727	1.6600	1.6239	1.5808	1.5432	1.5105	1.4823
20.0	1.8257	1.8118	1.7718	1.7238	1.6814	1.6442	1.6115
25.0	1.9860	1.9706	1.9263	1.8729	1.8254	1.7832	1.7459
30.0	2.1536	2.1367	2.0876	2.0283	1.9752	1.9278	1.8856
35.0	2.3289	2.3102	2.2559	2.1901	2.1311	2.0782	2.0307
40.0	2.5121	2.4914	2.4314	2.3586	2.2932	2.2343	2.1815
45.0	2.7035	2.6807	2.6145	2.5341	2.4617	2.3966	2.3379
50.0	2.9034	2.8783	2.8053	2.7167	2.6369	2.5650	2.5002
55.0	3.1123	3.0847	3.0043	2.9068	2.8190	2.7399	2.6686
60.0	3.3305	3.3001	3.2118	3.1046	3.0082	2.9214	2.8431
65.0	3.5586	3.5251	3.4281	3.3104	3.2048	3.1097	3.0240
70.0	3.7968	3.7601	3.6536	3.5246	3.4089	3.3050	3.2114
75.0	4.0459	4.0056	3.8886	3.7474	3.6210	3.5075	3.4054
80.0	4.3062	4.2620	4.1338	3.9792	3.8411	3.7174	3.6062
85.0	4.5784	4.5298	4.3894	4.2204	4.0697	3.9349	3.8141
90.0	4.8630	4.8098	4.6560	4.4713	4.3070	4.1603	4.0290
95.0	5.1608	5.1024	4.9340	4.7323	4.5533	4.3938	4.2512
100.0	5.4724	5.4084	5.2239	5.0037	4.8088	4.6355	4.4808

<sup>a</sup>  $A_H$  is in  $\text{J kg}^{1/2} \text{mol}^{-3/2}$ . <sup>b</sup> 1 atm.

$10^{-7}$ ) but lower than the values obtained from the KD equation ( $-4.806 \times 10^{-7}$  at 200 bar to  $-2.688 \times 10^{-7}$  at 1000 bar).

Thus, the Bradley and Pitzer (BP) equation (72) gives the dielectric constant of water at 1-atm pressure in excellent agreement with the IUPAC recommended values. In addition, the dielectric constant of water and its first and second derivatives with respect to temperature and pressure over the ranges 0–100 °C and 1–5 kbar as calculated from the BP equation are a good compromise between the UF and KD equations. The BP equation is the simplest of the four equations considered here because it does not require a knowledge of either the density or the saturation pressure of water. The UF and HK equations both require the density of the water before one can calculate its dielectric constant. The KD equation requires a prior knowledge of the saturation vapor

pressure in order to calculate  $D$ . Therefore, the BP equation can be considered as a very handy tool that fits the available experimental data fairly accurately. Therefore, it was used in calculating the limiting slope values presented in this work.

#### PVT Properties of Water

The PVT properties used in the present work were calculated by using the equations of Kell (28) and Chen, Fine, and Millero (29). The work of Kell and co-workers is the fundamental source of data for the Haar, Gallagher, and Kell (30) equation that was approved by the 9th International Association for the Properties of Steam (IAPS). Sato, Uematsu, and Watanabe (31) have observed that the data of Chen, Fine, and Millero are of high accuracy ( $\pm 0.002\%$ ) and are in good agreement with

Table VI. Pitzer-Debye-Hückel Slopes for the Apparent Molal Heat Capacity ( $10^{-2}A_J$ )<sup>a</sup>

temp/°C	press./bar						
	1 <sup>b</sup>	50	200	400	600	800	1000
0.0	0.254 25	0.254 65	0.254 99	0.254 11	0.251 81	0.248 23	0.243 48
5.0	0.269 77	0.269 16	0.266 77	0.262 88	0.258 24	0.252 89	0.246 90
10.0	0.284 46	0.283 10	0.278 66	0.272 52	0.266 09	0.259 38	0.252 41
15.0	0.298 82	0.296 88	0.290 83	0.282 88	0.275 01	0.267 19	0.259 39
20.0	0.313 21	0.310 77	0.303 37	0.293 89	0.284 79	0.276 00	0.267 46
25.0	0.327 83	0.324 96	0.316 35	0.305 51	0.295 31	0.285 63	0.276 41
30.0	0.342 85	0.339 57	0.329 85	0.317 74	0.306 49	0.295 98	0.286 10
35.0	0.358 36	0.354 70	0.343 89	0.330 56	0.318 29	0.306 95	0.296 41
40.0	0.374 46	0.370 41	0.358 53	0.343 98	0.330 69	0.318 52	0.307 31
45.0	0.391 22	0.386 79	0.373 81	0.358 00	0.343 67	0.330 64	0.318 73
50.0	0.408 71	0.403 87	0.389 75	0.372 63	0.357 23	0.343 31	0.330 67
55.0	0.426 99	0.421 72	0.406 39	0.387 91	0.371 37	0.356 51	0.343 09
60.0	0.446 11	0.440 38	0.423 77	0.403 84	0.386 10	0.370 24	0.355 99
65.0	0.466 14	0.459 91	0.441 93	0.420 45	0.401 43	0.384 50	0.369 37
70.0	0.487 13	0.480 38	0.460 92	0.437 77	0.417 37	0.399 29	0.383 22
75.0	0.509 16	0.501 38	0.480 76	0.455 82	0.433 93	0.414 63	0.397 52
80.0	0.532 30	0.524 34	0.501 52	0.474 63	0.451 15	0.430 52	0.412 30
85.0	0.556 61	0.547 96	0.523 24	0.494 24	0.469 03	0.446 96	0.427 53
90.0	0.582 19	0.572 79	0.546 00	0.514 69	0.487 60	0.463 97	0.443 21
95.0	0.609 13	0.598 90	0.569 83	0.536 02	0.506 88	0.481 55	0.459 33
100.0	0.637 54	0.626 40	0.594 81	0.558 27	0.526 90	0.499 70	0.475 88

<sup>a</sup>  $A_J$  is in  $\text{J kg}^{1/2} \text{mol}^{-3/2} \text{K}^{-1}$ . <sup>b</sup> 1 atm.

Table VII. Pitzer-Debye-Hückel Slopes for Apparent Molal Volume ( $A_V$ )

temp/°C	press./bar						
	1 <sup>b</sup>	50	200	400	600	800	1000
0.0	1.5061	1.4952	1.4620	1.4197	1.3797	1.3417	1.3056
5.0	1.5727	1.5601	1.5219	1.4735	1.4278	1.3846	1.3437
10.0	1.6420	1.6278	1.5848	1.5305	1.4793	1.4311	1.3855
15.0	1.7150	1.6991	1.6513	1.5911	1.5345	1.4812	1.4311
20.0	1.7922	1.7747	1.7220	1.6556	1.5935	1.5352	1.4804
25.0	1.8743	1.8550	1.7971	1.7245	1.6567	1.5932	1.5336
30.0	1.9616	1.9404	1.8772	1.7980	1.7242	1.6553	1.5907
35.0	2.0547	2.0315	1.9626	1.8765	1.7963	1.7216	1.6519
40.0	2.1540	2.1288	2.0537	1.9601	1.8732	1.7925	1.7172
45.0	2.2601	2.2326	2.1509	2.0493	1.9553	1.8680	1.7868
50.0	2.3734	2.3435	2.2547	2.1444	2.0426	1.9484	1.8609
55.0	2.4946	2.4620	2.3654	2.2458	2.1357	2.0339	1.9396
60.0	2.6242	2.5886	2.4836	2.3539	2.2347	2.1248	2.0233
65.0	2.7628	2.7240	2.6098	2.4691	2.3401	2.2214	2.1120
70.0	2.9111	2.8689	2.7446	2.5918	2.4521	2.3240	2.2061
75.0	3.0699	3.0238	2.8885	2.7226	2.5713	2.4329	2.3058
80.0	3.2400	3.1897	3.0422	2.8619	2.6981	2.5485	2.4115
85.0	3.4222	3.3672	3.2064	3.0104	2.8328	2.6711	2.5234
90.0	3.6175	3.5574	3.3820	3.1687	2.9761	2.8012	2.6419
95.0	3.8269	3.7612	3.5696	3.3374	3.1284	2.9393	2.7674
100.0	4.0517	3.9797	3.7702	3.5173	3.2905	3.0858	2.9004

<sup>a</sup>  $A_V$  is in  $\text{cm}^3 \text{kg}^{1/2} \text{mol}^{-3/2}$ . <sup>b</sup> 1 atm.

other contemporary data. In addition, the Haar, Gallagher, and Kell equation is nonlinear in density and cannot be solved directly. In view of this, the PVT properties of water at 1 atm were calculated by using the equation of Kell (28) and at other pressures up to 1 kbar by using the equation of Chen, Fine and Millero (29).

#### Definitions of the Limiting Slopes

There are some subtle differences among the various definitions of the limiting slopes as used by different workers such as Lewis and Randall (8), Helgeson and Kirkham (16), Redlich and Meyer (32), Millero (33), and Pitzer and co-workers (7, 12, 13). One minor difference is that the conventional  $A_\gamma$  (slope for activity coefficient) as used by Lewis and Randall is 2.3026 times smaller than the value used by Pitzer and co-workers

because Lewis and Randall use this  $A_\gamma$  in an expression for  $\log \gamma$  whereas Pitzer and co-workers use this in an expression for  $\ln \gamma$ . The  $A_H$ ,  $A_J$ ,  $A_V$ ,  $A_E$ , and  $A_K$  values used in the Pitzer formalism are smaller by a factor of  $2/3$  than the corresponding values used by the other workers. Bradley and Pitzer (12) justify this shift on the basis that this shift results in a unit numerical coefficient for 1:1 electrolytes for apparent molal functions. This definition of Bradley and Pitzer is in agreement with the definition of Redlich and Meyer (32) in the case of the slope for the apparent molal volume. Millero's (33) definition of  $S_V$  (slope for apparent molal volume) coincides with the Bradley-Pitzer (12) definition for  $A_V$ . However, Millero's (33) definitions for  $S_E$  and  $S_K$  do not coincide with the definitions (12) for  $A_E$  and  $A_K$ . These major trends in the definitions of Debye-Hückel slopes are summarized in Table I. It is essential to use an appropriate equation for a selected definition of the

Table VIII. Pitzer-Debye-Hückel Slope for Apparent Molal Expansivity ( $A_E$ )<sup>a</sup>

temp/°C	press./bar						
	1 <sup>b</sup>	50	200	400	600	800	1000
0.0	0.013 085	0.012 739	0.011 726	0.010 469	0.009 309	0.008 239	0.007 254
5.0	0.013 559	0.013 228	0.012 259	0.011 058	0.009 952	0.008 934	0.007 995
10.0	0.014 212	0.013 884	0.012 927	0.011 743	0.010 657	0.009 658	0.008 738
15.0	0.015 003	0.014 671	0.013 701	0.012 506	0.011 413	0.010 410	0.009 488
20.0	0.015 909	0.015 566	0.014 565	0.013 336	0.012 215	0.011 189	0.010 249
25.0	0.016 918	0.016 559	0.015 511	0.014 228	0.013 062	0.011 998	0.011 025
30.0	0.018 024	0.017 644	0.016 535	0.015 181	0.013 954	0.012 838	0.011 821
35.0	0.019 226	0.018 819	0.017 636	0.016 196	0.014 894	0.013 714	0.012 640
40.0	0.020 524	0.020 088	0.018 817	0.017 275	0.015 885	0.014 628	0.013 486
45.0	0.021 925	0.021 453	0.020 081	0.018 421	0.016 929	0.015 583	0.014 365
50.0	0.023 432	0.022 920	0.021 433	0.019 639	0.018 031	0.016 585	0.015 279
55.0	0.025 052	0.024 495	0.022 879	0.020 933	0.019 196	0.017 637	0.016 232
60.0	0.026 795	0.026 186	0.024 424	0.022 309	0.020 427	0.018 743	0.017 229
65.0	0.028 669	0.028 003	0.026 077	0.023 774	0.021 730	0.019 907	0.018 274
70.0	0.030 686	0.029 955	0.027 846	0.025 333	0.023 111	0.021 136	0.019 372
75.0	0.032 857	0.032 053	0.029 741	0.026 995	0.024 576	0.022 434	0.020 527
80.0	0.035 196	0.034 311	0.031 771	0.028 766	0.026 132	0.023 807	0.021 744
85.0	0.037 718	0.036 743	0.033 948	0.030 657	0.027 785	0.025 261	0.023 030
90.0	0.040 441	0.039 363	0.036 285	0.032 678	0.029 544	0.026 803	0.024 391
95.0	0.043 382	0.042 190	0.038 796	0.034 838	0.031 418	0.028 442	0.025 835
100.0	0.046 564	0.045 244	0.041 496	0.037 150	0.033 416	0.030 185	0.027 369

<sup>a</sup>  $A_E$  is in  $\text{cm}^3 \text{kg}^{-1} \text{mol}^{-1/2} \text{K}^{-1}$ . <sup>b</sup> 1 atm.

Table IX. Pitzer-Debye-Hückel Slopes for Apparent Molal Compressibility ( $10^4 A_K$ )

temp/°C	press./bar						
	1 <sup>b</sup>	50	200	400	600	800	1000
0.0	-2.0243	-2.2637	-2.1706	-2.0555	-1.9497	-1.8522	-1.7621
5.0	-2.3813	-2.6031	-2.4897	-2.3495	-2.2206	-2.1019	-1.9923
10.0	-2.7258	-2.9339	-2.7999	-2.6345	-2.4828	-2.3433	-2.2147
15.0	-3.0689	-3.2656	-3.1110	-2.9185	-2.7433	-2.5826	-2.4350
20.0	-3.4173	-3.6053	-3.4267	-3.2075	-3.0076	-2.8250	-2.6577
25.0	-3.7784	-3.9591	-3.7555	-3.5065	-3.2804	-3.0744	-2.8863
30.0	-4.1573	-4.3320	-4.1012	-3.8199	-3.5653	-3.3343	-3.1240
35.0	-4.5589	-4.7289	-4.4682	-4.1515	-3.8660	-3.6078	-3.3736
40.0	-4.9882	-5.1543	-4.8606	-4.5050	-4.1856	-3.8978	-3.6375
45.0	-5.4505	-5.6130	-5.2826	-4.8840	-4.5273	-4.2070	-3.9185
50.0	-5.9510	-6.1098	-5.7386	-5.2922	-4.8944	-4.5384	-4.2187
55.0	-6.4936	-6.6499	-6.2329	-5.7334	-5.2899	-4.8945	-4.5407
60.0	-7.0863	-7.2387	-6.7705	-6.2117	-5.7174	-5.2784	-4.8868
65.0	-7.7332	-7.8822	-7.3564	-6.7311	-6.1803	-5.6928	-5.2595
70.0	-8.4420	-8.5874	-7.9964	-7.2965	-6.6824	-6.1410	-5.6615
75.0	-9.2213	-9.3612	-8.6967	-7.9126	-7.2276	-6.6260	-6.0953
80.0	-10.078	-10.212	-9.4640	-8.5848	-7.8201	-7.1513	-6.5635
85.0	-11.023	-11.149	-10.306	-9.3190	-8.4646	-7.7205	-7.0690
90.0	-12.067	-12.183	-11.231	-10.1210	-9.1658	-8.3371	-7.6145
95.0	-13.221	-13.324	-12.248	-10.999	-9.9290	-9.0052	-8.2031
100.0	-14.500	-14.587	-13.367	-11.959	-10.760	-9.7287	-8.8375

<sup>a</sup>  $A_K$  is in  $\text{cm}^3 \text{kg}^{-1} \text{mol}^{-3/2} \text{bar}^{-1}$ . <sup>b</sup> 1 atm.

limiting slope. The equations of Pitzer and co-workers (1-7, 12-14) that employ the values of the slopes given in the present work are listed in Table II. Table III gives the detailed expressions used to evaluate the Pitzer-Debye-Hückel limiting slopes; Tables IV-IX give numerical values of the slopes to five significant figures.

The uncertainties in the Pitzer-Debye-Hückel limiting slopes reported here are dependent on the overall accuracy of (i) the dielectric constant and density of water and (ii) the first and second derivatives of the dielectric constant and density with respect to temperature and pressure. Fortunately, the volumetric properties of water in the range 0-100 °C and up to 1000-atm pressure are known very accurately (28-31) and consequently introduce only a small amount of error into the calculated values of the Pitzer-Debye-Hückel limiting slopes. The density of water over the temperature and pressure ranges considered in the present work are known with an accuracy of

$\pm 0.002\%$ . The maximum uncertainty in the thermal expansibility ( $\alpha$ ) and isothermal compressibility ( $\beta$ ) is estimated to be  $\pm 0.297\%$ . The estimated uncertainty in  $\partial^2 V/\partial T^2$ ,  $\partial \beta/\partial T$ , and  $\partial \beta/\partial P$  is about  $\pm 0.1\%$ . In comparison with the volumetric properties, the dielectric properties of water are known less accurately. The basic experimental accuracy of the experimental dielectric constants ranges from  $\pm 0.01\%$  (Lees (23)) to  $\pm 0.3\%$  (Heger (19)). A detailed analysis of the dielectric constant data for water has been done by several workers (12, 16, 17) and the dielectric constants calculated by using their equations agree to within  $\pm 0.1\%$ . The uncertainty in  $(\partial D/\partial T)_p$  values ranges from about  $\pm 1\%$  at 25 °C, 1-atm pressure to about  $\pm 2\%$  at 0 °C. The error in  $\partial^2 D/\partial T^2$  varies from  $\pm 3\%$  to about  $\pm 6\%$ . The error in  $(\partial D/\partial P)_T$  is estimated to be in the range  $\pm 2.5\%$  to  $\pm 5\%$  whereas the maximum error in  $(\partial^2 D/\partial P^2)_T$  is as high as  $\pm 15\%$ . On the basis of these uncertainties in the dielectric and volumetric properties of water the uncertainties in the Pitzer-Debye-Hückel parameters re-

ported in the present work were calculated to be as follows. The error in  $A_\phi$  and  $A_\gamma$  varies from a minimum of  $\pm 0.10\%$  at 25 °C and 1-atm pressure to a maximum of  $\pm 0.15\%$  at 100 °C and 1000-atm pressure. The uncertainty in  $A_H$  ranges from  $\pm 3\%$  at the minimum to a maximum of  $\pm 6.3\%$ . The largest uncertainty is in  $A_J$  and ranges from about  $\pm 3\%$  when component errors cancel each other to  $\pm 13.3\%$  when the errors are additive. The uncertainty in  $A_V$  ranges from  $\pm 0.25\%$  to  $\pm 0.5\%$ . The uncertainty ranges for  $A_E$  and  $A_K$  are respectively 0.8–1.0% and 1.0–1.7%. In view of these uncertainties it is recommended that  $A_\phi$  and  $A_V$  may be rounded off to four significant figures and the rest of the parameters to three significant figures for most practical work.

Registry No. Water, 7732-18-5.

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## Isobaric Vapor-Liquid Equilibria of the 6-Methyl-5-hepten-2-one/Ethyl 3-Oxobutanoate and Methanol/1,6-Hexanediol Systems

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**Isobaric vapor-liquid equilibria have been measured at 2.7 kPa for the 6-methyl-5-hepten-2-one/ethyl 3-oxobutanoate system and at 100.0 kPa for the methanol/1,6-hexanediol system. The experimental data have been obtained by using a new equilibrium still based on the flow method principle. Its main features, with respect to similar stills, are represented by the replacement of the Cottrell pump with a feed system that allows an independent control of overheating and of the liquid flow rate toward the equilibrium cell. The performance of the experimental apparatus has been checked by determining two literature systems.**

It is generally agreed that equilibrium stills based on flow methods are the most valuable tools available at present for vapor-liquid determinations (1). Fast reaching of equilibrium conditions, precise temperature determinations, and applicability to partially miscible systems are the main advantages offered by this type of instrument. If one puts aside Cathala's dynamic

ebullimeter because of several difficulties in its operation, the above-mentioned goals are perhaps realized in the most effective and simple way in an apparatus described by Vilim et al. (2). Such an apparatus is based on the assumption that equilibrium can be reached immediately, provided that the contact surface between the liquid and gas phases is large and the system is thermally insulated. These conditions are realized by means of an accurate control of overheating and of both the amount and the liquid/vapor ratio of the mixture fed to the equilibrium cell. Such a control can in turn be obtained by feeding the liquid phase to the Cottrell pump by means of hydraulic fall from a closed vessel through a float valve. In this way the amount of mixture fed to the equilibrium cell can be precisely replaced and the liquid level in the Cottrell pump kept constant. Fast attainment of equilibrium conditions is made possible through an adequate sizing of the equilibrium cell.

Despite the very good results obtained with this apparatus, the drawbacks caused by the Cottrell pump as a feeding element have not been eliminated, since the feed flow rate is always related to the overheating. Consequently, a separate