Refractive Index of Aqueous Electrolyte Solutions. Extrapolations to Other Temperatures, Pressures, and Wavelengths and to Multicomponent Systems

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An equation based on the Tamman-Tait-Gibson model for aqueous electrolyte solutions is used to extrapolate refractive index data to other wavelengths, temperatures, and pressures. These calculations and those made for multicomponent solutions show good agreement with experimental data. These results indicate how the extensive refractive index data for 20 °C and wavelength 5893 Å can be more widely utilized.

An equation was recently developed to predict the refractive index (RI) of aqueous electrolyte solutions (binary and mixed) to moderate pressures (ca. 1000 bar) (*5, 6*). This equation enabled estimates of seawater refractive index to be made up to 1000 bar from data at 1 bar, to an accuracy of 0.0001 or better (*7*). The seawater RI could also be predicted from binary solution data, which indicated that the equation could be used to predict the RI of mixed electrolyte solutions, at least up to moderate concentrations (ca. 1–2 *m* ionic strength).

There are very little RI data available on mixed aqueous solutions and even less at pressures other than atmospheric. In addition, a large bulk of the available RI data are for the Na D line (λ 5893 Å) and 20 °C. A useful feature of the above equation is that the *solute* parameters, besides being independent of pressure, are not very sensitive to wavelength or temperature so that predictions of the RI at other wavelengths and temperatures can be made from the Na D, 20 °C data. It is believed that the usefulness of the equation for extrapolating data is not well known and it is intended to illustrate this in the present paper. We give the RI estimates for mixtures of $CuSO_4$ and $ZnSO_4$ with H_2SO_4 and HCl, mixtures of KCl-HCl and NaCl-HCl, and pure solutions of KCl and NaCl. Comparative experimental data are available for these systems (*10, 11*). The aim is to illustrate how the RI equation can be used to extrapolate existing data to different wavelengths, temperatures and pressures, and mixtures of electrolytes. Such estimates of RI will be useful not only when experimental data are unavailable but also as a reference at the time measurements are being made.

Equations

The following equations are based on the Eisenberg RI equation for pure water (*1*) and on the Tammann-Tait-Gibson model for aqueous electrolyte solutions. They have been dealt with in detail previously (*5, 6*) so that only the details needed for their application are given.

The general equation for the *absolute* refractive index, *n*, is

$$f(n) = \frac{n^2 - 1}{n^2 + 2} = A(1/\psi_w)^B \exp(-Ct) + \Delta f(n) \qquad (1)$$

and

$$n = [(2f(n) + 1)/(1 - f(n))]^{1/2} \qquad (2)$$

Table I. Values of the Parameters *A*, *B*, and *C* of Equation 1, for Selected Wavelengths[a]

Wavelength, Å	*A*	*B*	10^5C
4046.6	0.211 952 6	0.876 42	6.5413
4358	0.210 535 2	0.878 98	6.5122
4880	0.208 749 7	0.881 89	6.4336
5461	0.207 306 3	0.884 10	6.3121
5892.6	0.206 470 9	0.885 38	6.2037
6328	0.205 769 1	0.885 42	6.0835
7065.2	0.204 786 2	0.887 96	5.8583

[a] For values at other wavelengths in the range 4046–7065 Å, see ref 5.

Table II. Solute Volumes and Coefficients[a]

	Volumes of "melted" solute		Coefficients[b] for eq 8	
Salt	$M\psi_s$, cm^3	ψ_s, cm^3/g	$10^2\ c_1$	$10^2\ c_2$
$BaCl_2$	56.8 ± 0.2	0.272	5.710 87	3.302 53
$CuSO_4$	41.6 ± 1	0.261	5.062 26	5.204 21
HCl	23 ± 1	0.631	10.807 7	
H_2SO_4	39 ± 1	0.398	5.695 81	3.664 27
KBr	42.5 ± 0.3	0.357	5.331 40	3.358 36
KCl	38.4 ± 1	0.515	4.857 15	1.472 34
K_2CrO_4	78.0 ± 0.4	0.402	8.622 97	3.463 61
LiCl	28.2 ± 0.4	0.665	7.493 90	−1.082 47
$MgSO_4$	44.3 ± 1.8	0.368	4.645 54	−0.717 324
NaBr	34.6 ± 0.4	0.336	5.744 49	3.936 69
NaCl	30.6 ± 0.5	0.522	5.693 38	0.004 33
Na_2CO_3	45.1 ± 1.9	0.425	4.237 44	−0.606 434
Na_2SO_4	59.4 ± 1.2	0.418	3.085 83	−2.247 92
$(NH_4)_2SO_4$	79.1 ± 0.6	0.599	5.622 16	1.410 26
$ZnSO_4$	40.7 ± 3	0.252	4.941 43	3.462 30

[a] See also, ref 5 and 6. [b] Derived from 20 °C RI data (*3*).

The first term on the right-hand side represents the contribution of the water in the solution; *t* is the temperature in °C; and *A*, *B*, and *C* are functions of the wavelength but independent of concentration, pressure, or temperature. Some representative values are given in Table I. These have been calculated from the polynomial in λ given by Leyendekkers (*5*), based on the results of Eisenberg (*1*). The quantity ψ_w is the apparent specific volume of the water in the solution and for any pressure, *p*, is given by

$$\psi_w^{(p)} = v_w^{(1)}[1 - 0.315 \log (B_T + p_e + p)/(B_T + 1)] \qquad (3)$$

with B_T, the Tait parameter, given by, from (*5*)

$$B_T = 2671.8 + 19.454t - 0.27028t^2 + 0.0009798t^3 \text{ (bar)} \qquad (3a)$$

and v_w, the specific volume of pure water, by (*2*)

$$v_w = (1/d_w)1.000028 \text{ cm}^3 \text{ g}^{-1}$$

with

$$d_w = 1 - (t - a_1)^2(t + a_2)/a_4(t + a_3) \text{ g mL}^{-1} \qquad (4)$$

for $0 \leqslant t \leqslant 40$ °C; with $a_1 = 3.9863$, $a_2 = 288.9414$, $a_3 = 68.12963$, and $a_4 = 508929.2$. Equation 4 gives equivalent values to those from the equation of Kell (*4*). p_e is the "effective

Table III. Comparison of Calculated and Experimental Refractive Indices of NaCl (Relative to Air)[a] at 25 °C, λ 6326 Å

c, mol/L of solution	m, mol/kg of water	x, g/g of solution	Exptl[b] a	Calcd b	10^4 ($b - a$)
0.0001	0.0001	0.000 006		1.331 25	
0.0005	0.0005	0.000 029		1.331 25	
0.001	0.001	0.000 059		1.331 26	
0.005	0.005	0.000 293		1.331 30	
0.01	0.010	0.000 59	1.331 26	1.331 35	0.9
0.02	0.020	0.001 17	1.331 40	1.331 45	0.5
0.03	0.030	0.001 76	1.331 51	1.331 54	0.3
0.05	0.050	0.002 92	1.331 72	1.331 75	0.3
0.10	0.100	0.005 84	1.332 16	1.332 25	0.9
0.20	0.201	0.011 63	1.333 13	1.333 25	0.9
0.50	0.506	0.028 72	1.336 28	1.336 26	−0.2
1.00	1.022	0.056 35	1.341 30	1.341 02	−2.8
1.45	1.500	0.080 60		1.345 19	
1.50	1.549	0.082 99		1.345 67	
1.920	2.0	0.104 65	1.349 3	1.349 37	0.7 (8.2)[c]
3.687	4.0	0.189 47	1.364 1	1.364 32	2.2 (6.8)[c]
5.302	6.0	0.259 61	1.377 1	1.376 92	−1.8 (5.8)[c]

[a] The calculated values were divided by 1.000 29 to convert from the absolute values. [b] References 10 and 11. [c] Reference 9, possible experimental deviations due to limiting accuracy of solution composition, viz. ±0.1 m.

Table IV. Coefficients[a] for the Equations $\phi_v = a_0 + a_1m^{1/2} + a_2m + a_3m^{3/2} + a_4m^2$, cm^3/mol; $\phi_v = \phi_v^0 + s_vc^{1/2}$, mL/mol; $p_e = h_0 + h_1x + h_2x^2 + h_3x^3 + h_4x^4$ (bar), t = 25 °C

Salt	ϕ_v^0, s_v	a_0, a_1, a_2	a_3, a_4	h_0, h_1, h_2	h_3, h_4, std dev (±)
NaCl	16.40, 2.153	16.617, 1.850, 0.05		0.497, 4954.68, 1.600	18106.2, −27448.5, 0.19
KCl	26.52, 2.327	26.85, 1.802, 0.135		0.399, 3190.36, −1292.78	9760.81, −21184.4, 0.14
$MgSO_4$		−7.180, 35.44, −73.72	98.4, −48.8	1.39, 8166.80, 11415.9	−260745, 2511740, 0.34
HCl	18.07, 0.950	18.069, 0.9576, −0.0163		0.320, 2700.53, −6198.60	27119.0, −65972.1, 0.14

[a] Coefficients of p_e equation are independent of pressure and wavelength.

Table V. Coefficients[a] for the equation $p_e = h_0 + h_1x_2 + h_2x_2^2 + h_3x_2^3$ (bar), t = 20 °C

Salt	h_0	h_1	h_2	h_3	Std dev (±)
Nacl	−0.03	5078.65	2.022	11206.30	0.3
KCl	0.51	3276.21	−1549.34	6344.26	0.1
HCl	1.000	2596.95	−734.855		0.01
H_2SO_4	3.64	1186.78	−4320.32	3786.77	1.2
$CuSO_4$	−3.95	6698.97	−6107.14	38950.0	1.5
$ZnSO_4$	−4.02	6406.27	−5025.18	37898.2	0.7

[a] Independent of pressure and wavelength.

pressure'' exerted by the solute on the water and is a function of temperature and concentration but independent of pressure. p_e is related to the compressibility of the solution via the Tait–Gibson equation,

$$\beta^{(p)}v^{(p)} = 0.4343x_1\,(0.315v_w^{(l)})/(B_T + p_e + p) \qquad (5)$$

with x_1 representing the grams of water per gram of solution and β the isothermal compressibility coefficient ($-(1/v)\,(\partial v/\partial p)_T$). Another relationship for ψ_w is

$$\psi_w = (v - x_2\psi_s)/x_1 \qquad (6)$$

with v the specific volume of the solution and x_2 the number of grams of solute in 1 g of solution. The quantity ψ_s is the specific volume of the solute (as a liquid). Equation 6 is a very convenient equation as density data (in the form of the apparent molal volume, ϕ_v, functions) are available for a large range of electrolytes and ψ_s is also available for many electrolytes. This latter quantity is fairly insensitive to temperature or concentration (*5*). When ψ_w has been calculated, the corresponding values of p_e can then be derived via eq 3. Alternatively, p_e can be derived from eq 5 (preferably with data for $p \geqslant 300$ bar) and thence ψ_w can be calculated from eq 3.

For a mixture of electrolytes, the total "effective pressure" of the solute, P_e, is simply given by

$$P_e = \Sigma_i p_{e,i} \qquad (7)$$

where $p_{e,i}$ is the value for the binary solution of i with solute concentration x_i g/g of solution, the same as in the mixed solution. The second term on the right-hand side of eq 1, $\Delta f(n)$, represents the contribution of the solute. This term changes negligibly with pressure to moderate pressures (ca. 1000 bar) and is only slightly sensitive to wavelength and temperature changes. For concentrations up to about 0.25 g/g of solution, $\Delta f(n)$ can be represented by

$$\Delta f(n) = c_1x + c_2x^2 \qquad (8)$$

for mixed electrolyte solutions

$$\Delta f(n) = \Sigma_i(c_{1,i}x_i + c_{2,i}x_i^2) \qquad (9)$$

Extrapolation of RI Data

As noted above, there are extensive data on the RI of aqueous solutions at 20 °C for the Na-D line (λ 5893 Å) (*3*). These data have been used as a basis for deriving values of c_1 and c_2 of eq 8 for a number of electrolytes of diverse types (*6*). Values of $M\psi_s$ (the molal volume of the *liquid* solute) and ψ_s were also derived (Table II), and these can be used in eq 6, together with specific volume data, to estimate ψ_w at 25 °C. The first term of eq 1 can thus be calculated for 25 °C for any wavelength, using the appropriate values of A, B, and C (Table I). The value of $\Delta f(n)$ does not change very much with wavelength nor with temperature (*7*) so that a good estimate of the second term of eq 1 could be expected from eq 8 using the coefficients listed in Table II. We have estimated values of the RI of NaCl, KCl, HCl, and $MgSO_4$ at various wavelengths in this way and compare the results with experimental data. Table III lists the values for NaCl. To save space, the results for the other salts are given later (see Tables VI and IX). The specific volumes were obtained from the ap-

Table VI. Calculated Refractive Index of Aqueous KCl–HCl Solutions (Relative to Air),[a] $t = 25$ °C, λ 6328 Å

KCl, mol/L	HCl, mol/L					
	0	0.0001	0.001	0.01	0.1	1.0
0				1.33133 (−3)	1.33209 (−5)	1.33950
0.0001	1.33124 (−3)	1.33127 (0)	1.33127 (−1)	1.33135 (2)	1.33211	1.33951
0.0005	1.33124 (−3)	1.33127 (5)	1.33128	1.33135 (1)	1.33211	1.33951
0.001	1.33125 (−2)	1.33127 (0)	1.33128 (1)	1.33136	1.33212	1.33952 (12)
0.002	1.33126 (−1)	1.33128 (1)	1.33129 (2)	1.33137	1.33213	1.33953
0.005	1.33129 (1)	1.33131 (1)	1.33132	1.33140 (2)	1.33216	1.33955
0.01	1.33134 (1,8)	1.33136 (1)	1.33137	1.33145	1.33220 (−1)	1.33960 (1)
0.02	1.33144 (4,4)	1.33146	1.33147 (2)	1.33154	1.33230	1.33969
0.05	1.33173 (1,1)	1.33175	1.33176 (4)	1.33184 (5)	1.33259	1.33997 (2)
0.10	1.33223 (5,7)	1.33224	1.33225 (4)	1.33233 (8)	1.33308 (4)	1.34043
0.20	1.33321 (−6,8)	1.33322	1.33322 (−6)	1.33330 (−6)	1.33405 (−3)	1.34135 (−20)[b]
0.30	1.33419 (−6,−)	1.33418	1.33419	1.33427	1.33501	1.34227 (−36)[b]
0.50	1.33611 (31,−17)	1.33610	1.33611	1.33618	1.33691	1.34408
1.00	1.34080 (−8,−3)	1.34080	1.34080	1.34088	1.34159	1.34854
1.50	1.34534	1.34535	1.34536	1.34543	1.34612	1.35287

[a] Values in parentheses are deviations $(n_{\text{calcd}} - n_{\text{exptl}}) \times 10^5$, experimental data from ref 11 where two values are shown, second is from ref 10, corrected in ref 11. [b] These deviations based on assumption that experimental values listed under 0.1, 0.2 M KCl (Table I or ref 11) should be 0.2, 0.3 M, respectively.

Table VII. Calculated Refractive Index of Aqueous KCl–HCl and NaCl–HCl Solutions (relative to air), $t = 20$ °C, λ 6328 Å

KCl (a) or NaCl (b), mol/kg of water		HCl, mol/kg of water				
		0.0001	0.001	0.01	0.1	1.0
0.0005	a,b	1.331 75	1.331 75	1.331 83	1.332 59	1.339 88
0.001	a,b	1.331 75	1.331 76	1.331 83	1.332 59	1.339 89
0.002	a,b	1.331 76	1.331 77	1.331 84	1.332 60	1.339 89
0.005	a,b	1.331 79	1.331 80	1.331 87	1.332 63	1.339 92
0.01	a,b	1.331 84	1.331 85	1.331 93	1.332 68	1.339 97
0.02	a,b	1.331 94	1.331 95	1.332 03	1.332 78	1.340 06
0.05	a,b	1.332 24	1.332 25	1.332 33	1.333 08	1.340 33
0.1	a	1.332 74	1.332 75	1.332 83	1.333 57	1.340 78
	b	1.332 76	1.332 77	1.332 84	1.333 59	1.340 81
0.2	a	1.333 73	1.333 74	1.333 81	1.334 55	1.341 68
	b	1.333 78	1.333 78	1.333 86	1.334 60	1.341 74
0.3	a	1.334 70	1.334 71	1.334 78	1.335 51	1.342 56
	b	1.334 78	1.334 79	1.334 86	1.335 59	1.342 66
0.5	a	1.336 60	1.336 61	1.336 68	1.337 39	1.344 28
	b	1.336 74	1.336 75	1.336 82	1.337 54	1.344 47
1.0	a	1.341 13	1.341 14	1.341 21	1.341 88	1.348 39
	b	1.341 45	1.341 45	1.341 52	1.342 20	1.348 79

Table VIII. Calculated Effect of HCl and H_2SO_4 on the Refractive Index (abs) of $CuSO_4$ and $ZnSO_4$, $t = 20$ °C, λ 5893 Å

mol/kg of water	n_0[a]	$10^5 (n_{\text{mix}} - n_0)$						
		HCl				H_2SO_4		
		0.1	0.05	0.02	0.01	0.05	0.01	0.005
$CuSO_4$								
0.75	1.353 77	69	35	15	8	47	14	9
0.70	1.352 50	70	36	15	8	48	14	9
0.60	1.349 93	72	36	15	8	50	14	9
0.50	1.347 32	74	37	16	8	52	14	9
0.40	1.344 66	76	38	16	9	54	15	10
0.30	1.341 94	78	40	17	9	57	15	10
0.20	1.339 15	81	41	17	9	59	16	10
0.16	1.338 01	82	41	17	9	60	16	11
0.10	1.336 27	83	42	18	10	61	16	11
0.08	1.335 68	84	43	18	10	62	16	11
$ZnSO_4$								
0.15	1.337 61	80	40	16	8	55	11	5
0.10	1.336 20	81	41	16	8	56	11	5
0.08	1.335 62	82	41	17	9	57	12	6
0.05	1.334 75	83	42	17	9	58	12	6
0.01	1.333 58	84	42	17	9	58	12	6
0.005	1.333 43	84	42	17	9	58	12	6

[a] Interpolated experimental values (*3*), multiplied by 1.00029 to convert to absolute values.

Table IX. Calculated Refractive Index (abs) of Aqueous NaCl and $MgSO_4$ for 1–400 Bar at 25 °C,[a] $n^{(p)} = n^{(1)} + p(\partial n/\partial p)_T$

m	$n^{(1)}$ and $(\partial n/\partial p)_T \times 10^6$ bar^{-1} (10^{11} m^2 N^{-1})							
	λ 6328 Å		λ 5461 Å		λ 4861 Å		λ 4358 Å	
NaCl								
0.11	1.33274	14.01	1.33545	14.12	1.33811	14.21	1.34120	14.31
0.86	1.33992	13.44	1.34266	13.55	1.34535	13.63	1.34847	13.73
						13.6[b]		
1.00	1.34119	13.35	1.34394	13.45	1.34663	13.54	1.34976	13.63
1.51	1.34567	13.02	1.34844	13.12	1.35115	13.20	1.35429	13.30
						12.9[b]		
1.90	1.34894	12.79	1.35173	12.89	1.35445	12.97	1.35760	13.06
2.00	1.34976	12.72	1.35255	12.83	1.35527	12.91	1.35843	13.00
	(1.3497)	(12.45)	(1.3527)	(12.57)			(1.3592)	(12.90)
2.10	1.35058	12.67	1.35337	12.77	1.35609	12.85	1.35926	12.94
3.00	1.35757	12.20	1.36039	12.30	1.36314	12.37	1.36633	12.46
3.90	1.36403	11.79	1.36688	11.88	1.36965	11.95	1.37288	12.04
4.00	1.36472	11.74	1.36757	11.84	1.37035	11.91	1.37357	12.00
	(1.3645)	(10.74)	(1.3678)	(11.15)			(?)	(11.02)
4.10	1.36540	11.70	1.36826	11.79	1.37104	11.87	1.37426	11.95
5.00	1.37128	11.35	1.37417	11.43	1.37697	11.51	1.38022	11.59
5.90	1.37674	11.03	1.37964	11.12	1.38246	11.19	1.38574	11.27
6.00	1.37732	11.00	1.38023	11.08	1.38305	11.16	1.38633	11.24
	(1.3775)	(10.13)	(1.3810)	(9.96)			(1.3885?)	(10.16)
6.10	1.37789	10.97	1.38080	11.05	1.38363	11.12	1.38691	11.20
$MgSO_4$								
0.11	1.33429	14.34	1.33701	13.89	1.33968	13.98	1.34278	14.08
						14.3[b]		
0.20	1.33640	13.53	1.33913	13.64	1.34181	13.73	1.34492	13.82
						14.1[b]		
0.33	1.33933	13.21	1.34208	13.31	1.34477	13.39	1.34789	13.49
						13.7[b]		
0.86	1.35074	12.01	1.35355	12.10	1.35629	12.18	1.35948	12.27
0.91	1.35187	11.89	1.35469	11.98	1.35744	12.06	1.36063	12.14
						12.2[b]		
1.00	1.35398	11.67	1.35682	11.76	1.35957	11.83	1.36277	11.92
	(1.3528)	(12.25)	(1.3561)	(12.13)			(1.3620)	(12.46)
1.10	1.35646	11.41	1.35931	11.50	1.36207	11.57	1.36529	11.65

[a] Values in parentheses are experimental (*9*); N.B. experimental concentrations are ±0.1 *m*. [b] Other theoretical estimates (*8*) are for λ 4881 Å.

parent molal volume functions (*5, 12*). For ϕ_v expressed as a function of the molality (mol/kg of water), usually as a polynomial in $m^{1/2}$ (Table IV), the specific volume is given by

$$v = (m\phi_v + 10^3 v_w)/(10^3 + mM) \qquad (10)$$

where M is the molecular weight of the salt. When ϕ_v is expressed in the form

$$\phi_v = \phi_v{}^0 + s_v c^{1/2} \qquad (11)$$

with c the number of moles/liter of solution, then $v = 1/d$, with

$$d = d_w + (M - d_w\phi_v{}^0)10^{-3}c - (s_v d_w)c^{3/2}10^{-3} \qquad (12)$$

and d_w represents the density of pure water. A useful interconversion equation for the two concentration scales (for binary solutions) is

$$m = c/[d_w(1 - 10^{-3}c\phi_v)] \qquad (13)$$

In general, the estimates are in good agreement with the experimental data. The exceptions appear to indicate deficiencies in the experimental values (see, e.g., KCl results at 0.5 M, Table VI). The experimental values for the higher concentrations, 2–6 *m*, are associated with possible deviations in solution concentration of ±0.1 *m* (*9*) so that the agreement in this case is considered satisfactory. This also applies to the $MgSO_4$ results.

Mixtures of Salts with Strong Acids

Values of p_e were calculated from ψ_w via eq 3 and 3a and fitted to x_2 for NaCl, KCl, HCl, and $MgSO_4$ at 25 °C. The method of calculating ψ_w was outlined in the previous section. The values of the p_e functions are listed in Table IV. Corresponding values for H_2SO_4, HCl, $CuSO_4$, and $ZnSO_4$ were also derived for 20 °C (Table V). The total effective pressure for mixtures of salts and acids can thus be calculated from eq 7. Values of $\Delta f(n)$ can be calculated from eq 8. The RI of the mixture is then calculated via eqs 3, 3a, and 1. The results for KCl–HCl are listed in Table VI together with the deviations from the experimental data. In general, the deviations are within the experimental errors. The two notable exceptions are for the mixtures 1 M HCl with 0.1 and 0.2 M KCl. Graphical interpolation, together with our results suggest that the concentrations of KCl are 0.2 and 0.3 M, respectively, rather than 0.1 and 0.2 M as listed in ref 11. Even so, the deviations are still somewhat high. This is partly due to the difficulty of converting from the molal (mol/kg of water) scale on which our equations are based to the molar (mol/L of solution) scale used for the experimental data. We have used the extension of eq 13 for a two-electrolyte mixture, viz.

$$m_A = c_A/(d_w(1 - 0.001[c_A\phi_v(A) + c_B\phi_v(B)])) \qquad (14)$$

(For calculation of ϕ_v in mixture see ref 5 or use binary solution value at ionic strength of mixture.) and similarly for B, with $x_A = m_A M_A/(m_A M_A + m_B M_B + 10^3)$. The corresponding values of the RI for NaCl–HCl mixtures are similar to those for KCl. Table VII lists values calculated for 20 °C for these two salts. The effects of HCl and H_2SO_4 on $CuSO_4$ and $ZnSO_4$ at 20 °C are summarized in Table VIII. The effect of the two acids is compared on the basis of the stoichiometric concentration of the hydrogen ion. O'Brien (*10*) has measured the RI of these salts as a function of pH. The systems he studied contained H_2SO_4 and/or NaOH (concentrations unspecified) and the temperature was at 25 °C so that direct comparison is not possible. However, the magnitudes of the acid effect, as indicated in Table VIII, are consistent with his results. For example, at a pH of 1.1, at 25 °C and concentrations of $CuSO_4$ of 0.4, 0.16, and 0.08 M, the changes in the experimental RI were 96, 96, and 83 × 10^{-5}, respectively.

Pressure Effects

As noted above, it has been shown that the effect of pressure on the RI of a mixed electrolyte solution such as seawater (ionic strength maximum around 0.85 *m*) can be predicted by eq 1 to 0.0001 or better (*7*). There does not seem to be any RI data for other mixed electrolyte solutions under pressure. However, on the basis of the seawater results it might be expected that reasonable estimates of the RI would be obtained at moderate concentrations (to 1 or 2 *m*, say). When data on p_e and $\Delta f(n)$ are available (or data to calculate them) the value of the RI at a pressure p is simply obtained from eq 1, using $\psi_w^{(p)}$ from eq 3 and then eq 2. Extensions to the mixed solutions are made using eq 7 and 9 as well. Values of n for NaCl and $MgSO_4$ at 25 °C and pressures to 400 bar were calculated for a range of concentrations. The values were fitted to p at each concentration (linear fit with standard deviation 2 × 10^{-5}). The piezo-optic coefficient, $(\partial n/\partial p)_T$, was thus the slope of the lines. Comparison of this coefficient with direct experimental values (*9*) gives an indirect check on the reliability of n at the elevated pressures. The results are summarized in Table IX from which the value of n for a given concentration at any pressure up to 400 bar can be calculated. At moderate concentrations the agreement with experiment is good, but at 4-6 *m* the values of n predicted at 400 bar could be in error by 4 × 10^{-4} for the wavelengths 6328-5461 Å. As the differences in the given wavelength and 5893 Å increase, the errors, arising from the assumption that $\Delta f(n)$ is independent of wavelength naturally increase. Thus, for λ 4358 Å the errors at the higher concentrations apparently become as great as 8 × 10^{-4}. It should be noted that the experimental concentrations are only accurate to 0.1 *m* and we have included extra n and $(\partial n/\partial p)_T$ values to indicate the possible errors in n and $(\partial n/\partial p)_T$ from this source. While not being very significant for NaCl, the greater sensitivity of the parameters to concentration for $MgSO_4$ gives larger experimental uncertainties for this salt. At low concentrations the experimental data have been supplemented with estimates of $(\partial n/\partial p)_T$ made from other, more restrictive models (i.e., models not so easily applicable to multicomponent solutions) (*8*). These values, too, are in accord with our results.

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A Simple Formula for the Heat Capacity of Polyatomic Gases, with Constants for 143 Substances

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A simple empirical formula, $c_v \sim x^2/(1 + x^2)$, is suggested for the representation of ideal-gas heat capacities. There are only two empirical constants, B and τ, contained in the definition $x = B(\hat{T} - \tau)$; both have a physical interpretation. The suggested form has the advantages of simplicity and fidelity over a large temperature range. Fitted constants for 143 substances are presented.

Ideal-gas heat capacities are commonly represented by polynomials in the absolute temperature T, with coefficients empirically fitted to the data for each substance. A typical form is

$$c_p{}^0 = a + bT + cT^2 + dT^3 \tag{1}$$

where $c_p{}^0$ is the zero-pressure heat capacity at constant pressure in cal/(mol K) and T is in kelvins. The constants a, b, c, and d are tabulated for 102 substances by Hougen, Watson, and Ragatz (*7*); there are, of course, many such tabulations. The polynomial representation is quite convenient, the integrations for enthalpy and entropy being very simple. The representation is also accurate, provided that the temperature limits of the range over which the polynomial was fitted are not exceeded.

An alternative empirical representation, the subject of this paper, is the form $c_p{}^0 \sim y$, with

$$y = x^2/(1 + x^2) \tag{2}$$

where x is a linear function of temperature. The function $y(x)$ is plotted in Figure 1. The rationale is that the increase in y with x corresponds to the excitation of vibrational degrees of freedom with increasing temperature: thus $y = 0$ corresponds to no vibrational excitation and $y = 1$ corresponds to full vibrational excitation. In terms of the reduced ideal-gas heat capacity at constant volume $\hat{c}_v \equiv c_v{}^0/R$, the explicit form is then

$$\begin{aligned} y &= \frac{\hat{c}_v - c_\alpha}{c_\omega - c_\alpha} = \frac{x^2}{1 + x^2} \qquad (x \geq 0) \\ y &= \frac{\hat{c}_v - c_\alpha}{c_\omega - c_\alpha} = 0 \qquad (x < 0) \end{aligned} \tag{3}$$

where c_α is the constant-volume heat capacity with translational and rotational degrees of freedom only ($y = 0$), c_ω is the con-