

Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Bi-Univalent Compounds of Lead, Copper, Manganese, and Uranium

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A critical evaluation of the mean activity and osmotic coefficients in aqueous solutions of twelve bi-univalent compounds of lead, copper, manganese and uranium at 298.15 K is presented. Osmotic coefficients were calculated from direct vapor pressure measurements, from isopiestic measurements and from freezing point depression measurements. Activity coefficients were calculated from electromotive force measurements on galvanic cells without transference. Given are empirical coefficients for three different correlating equations, obtained by a weighted least squares fit of the experimental data, and tables consisting of the activity coefficients of the compounds, the osmotic coefficients and activity of water, and the excess Gibbs energy of the solution as functions of the molality for each electrolyte system. The literature coverage is through the computerized version of Chemical Abstracts of April 1979.

Keywords: Activity coefficient; copper; critical evaluation; electrolyte; excess Gibbs energy; lead; manganese; osmotic coefficients; solutions; thermodynamic properties; uranium.

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1. Introduction

This paper presents a continuation of work at the National Bureau of Standards towards the evaluation of activity and osmotic coefficients in aqueous solutions. Previously, evaluations have been made for the uni-univalent electrolytes [1]¹, calcium chloride [2], the alkaline earth metal halides [3], sulfuric acid [4], and FeCl₂ and the bi-univalent compounds of iron, nickel, and cobalt [5]. The evaluation procedures have been described [2,3,6] in substantial detail and a bibliography [7] giving the results

¹ Figures in brackets indicate literature references.

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of a search of the scientific literature for relevant sources of experimental data has been published.

We present our evaluations in detail so that any potential users of the data, as well as future data evaluators, can have a better view of the status of the measurements on these systems. We also give coefficients, obtained by a weighted least-squares fit of the experimental data, for three different correlating equations and tables consisting of the mean activity coefficients of the electrolyte, the osmotic coefficient and activity of water, and the excess Gibbs energy of the solution as functions of the molality for each electrolyte system at 298.15 K. The literature coverage is through the computerized version of Chemical Abstracts of April 1979.

The reader is referred to the glossary of symbols at the end of this paper for the definitions of the various sym-

bols used throughout this paper. In general, we have attempted to adhere to the recommendations of the IUPAC [8] with regard to nomenclature and units.

2. Evaluated Activity and Osmotic Coefficients

2.1. Presentation of Data

We have arranged the presentation of data according to compound. For each compound that has been evaluated we present:

1. The recommended values of the activity and osmotic coefficients, the activity of water, and the excess Gibbs energy per kilogram of solvent at selected molalities, including, where possible, values at saturation. The latter molalities, indicated by (sat) in the tables, were calculated from the data given in the compilation of Linke and Seidell [9]. Estimates of the standard deviations of the calculated values of the osmotic coefficient $[\sigma(\phi)]$, the activity coefficient $[\sigma(\gamma)]$, and the natural logarithm of the activity coefficient $[\sigma(\ln \gamma)]$, all at selected molalities, are given at the bottom of each table.

2. The coefficients, standard deviations of the coefficients $[\sigma(\text{coeff})]$, and standard deviation for observations of unit weights $[\sigma(\text{eqtn})]$ for as many as three different correlating equations. The correlating equations we have used are:

$$\ln \gamma = -\frac{A_1 I^{1/2}}{1 + BI^{1/2}} + Cm + Dm^2 + Em^3 + \dots, \quad (1a)$$

$$\ln \gamma = -A_1 I^{1/2} - A_2 I \ln I + \sum_{i=1}^N B_i m^{(i+1)/2}, \quad (2a)$$

$$\ln \gamma = -A_1 I^{1/2} + \sum_{i=1}^N B_i m^{(i+1)/2} \quad (3a)$$

The corresponding equations for the osmotic coefficient become:

$$\begin{aligned} \phi = 1 + \frac{A_1}{B^2 I} \{ & -(1 + BI^{1/2}) + 2 \ln(1 + BI^{1/2}) + \\ & 1/(1 + BI^{1/2}) \} + \\ & \frac{1}{2} Cm + \frac{2}{3} Dm^2 + \frac{3}{2} Em^3 + \dots, \end{aligned} \quad (1b)$$

$$\phi = 1 - \frac{A_1}{3} I^{1/2} - \frac{A_2}{2} I [\ln I + \frac{1}{2}] +$$

$$\sum_{i=1}^N B_i \frac{(i+1)}{(i+3)} m^{(i+1)/2} \quad (2b)$$

and

$$\phi = 1 - \frac{A_1}{3} I^{1/2} + \sum_{i=1}^N B_i \frac{(i+1)}{(i+3)} m^{(i+1)/2}. \quad (3b)$$

For 2-1 electrolytes in water at 25 °C, $A_1 = 2.3525 \text{ mol}^{-1/2} \cdot \text{kg}^{1/2}$ and $A_2 = \frac{2}{3} A^2 = 0.92238 \text{ mol}^{-1} \cdot \text{kg}$ and A is the constant in the Debye-Hückel equation and is equal to $1.17625 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ at 25 °C. The user should note that in our tables, where we have given the coefficients of these correlating equations for the various systems that have been evaluated, we have used a shorthand notation to designate the various parameters, i.e., parameter 1 corresponds to either B in eqs 1, or B_1 in eqs 2 or 3, parameter 2 corresponds to either C in eqs 1 or B_2 in eqs 2 or 3, parameter 3 corresponds to either D in eqs 1 or B_3 in eqs 2 or 3, etc. Also, powers of ten are implied in the representation of a number, e.g., 0.499-02 is 0.499×10^{-2} . We have retained ten digits for the coefficients in order to avoid a loss of potentially useful information which might be of value for some applications in which the derivative of the activity coefficient with respect to the molality is of interest. The digits in excess of those required to ensure a precision of 0.001 or better in the calculation of ϕ or $\ln \gamma$ have not been underlined. Unless indicated otherwise the coefficients for eqs (1a) and (1b) were used to produce the activity and osmotic coefficients given in the tables of recommended values.

3. The calculated values of ϕ and/or $\gamma/\gamma_{\text{ref}}$ obtained from the experimental measurement reported by the various authors and the weights assigned to the various data sets. It should be noted that, in most cases, these are not original data, but rather the result of an intermediate calculation. Individual data points designated by an asterisk (*) were given zero weight.

and

4. A deviation plot in $\Delta\phi$ and/or $\Delta\gamma$ as a function of the molality. In these plots the symbol Δ means "observed minus calculated" values.

The excess Gibbs energy ΔG^{ex} , is given by $\Delta G^{\text{ex}} = G - G_{\text{ideal}} = \nu mRT(1 - \phi + \ln \gamma)$.

2.2. Evaluated Systems

PbCl₂Recommended Values for the mean activity and osmotic coefficient of PbCl₂ in H₂O at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8548	.9447	.999949	-1.
.002	.7970	.9209	.999900	-2.
.003	.7565	.9041	.999853	-4.
.004	.7252	.8912	.999807	-6.
.005	.6997	.8808	.999762	-9.
.006	.6782	.8721	.999717	-12.
.007	.6596	.8646	.999673	-15.
.008	.6432	.8580	.999629	-18.
.009	.6285	.8520	.999586	-21.
.010	.6152	.8465	.999543	-25.
.020	.5197	.7991	.999137	-67.
.030	.4541	.7542	.998778	-121.
.039 (sat)	.4118	.7256	.998468	-178.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0006	.0016	.0014
.010	.0022	.0030	.0018
.100	.7012	.8673	1.8686
.039	.0058	.0059	.0024

Coefficients of Correlating Equations

Par	Eqs 2		Eqs 3	
	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$
1	-.6625917316+02	.376+01	-.4630334060+02	.377+01
2	.8502334591+03	.903+02	.6909273162+03	.905+02
3	-.4469254073+04	.686+03	-.3776846012+04	.687+03
4	.8390746759+04	.165+04	.7148607276+04	.166+04

$$\sigma(\text{eqs 2}) = .841-02$$

$$\sigma(\text{eqs 3}) = .843-02$$

Experimental Data Employed in Generation of Correlating Equations

Allmand and Hunter [15]. Emf measurements. Pb(Hg)_x(l); PbCl₂(m); AgCl(s), Ag(s). $m_{\text{ref}} = 0.0010 \text{ mol}\cdot\text{kg}^{-1}$. Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\gamma/\gamma_{\text{ref}}$
.039084	.4806
.031623	.5245
.025119	.5694
.019953	.6135
.015849	.6524
.012589	.6903
.010000	.7265
.007943	.7607
.006310	.7882
.005012	.8168
.003981	.8398
.003162	.8681
.002512	.8970
.001995	.9249
.001585	.9509
.001259	.9751
.001000	1.0000
.000794	1.0176
.000631	1.0381
.000501	1.0563
.000398	1.0722*

Allmand and Hunter [15]. (Continued)

$m/\text{mol}\cdot\text{kg}^{-1}$	$\gamma/\gamma_{\text{ref}}$
.000316	1.0996*
.000251	1.1188*
.000200	1.1445*
.000158	1.1705*
.000126	1.2035*
.000100	1.2569*
.0000794	1.3166*

Carmody [16]. Emf measurements. Pb(Hg)_x(l); PbCl₂(m); AgCl(s), Ag(s). $m_{\text{ref}} = 0.0002116 \text{ mol}\cdot\text{kg}^{-1}$. Assigned weight is 1.0.

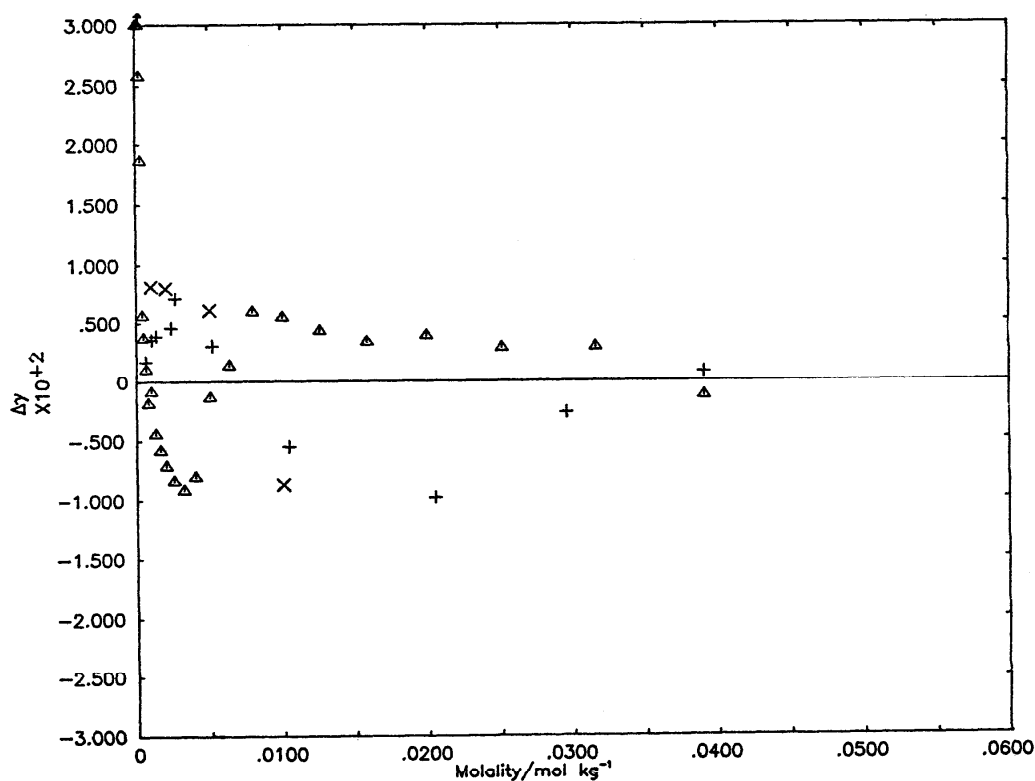
$m/\text{mol}\cdot\text{kg}^{-1}$	$\gamma/\gamma_{\text{ref}}$
.000620	.9495
.001034	.9150
.001337	.8939
.002348	.8400
.002620	.8308
.005160	.7467
.010390	.6463
.020480	.5411
.029550	.4849
.039050	.4412

Hannan [17]. Emf measurements. $\text{Pb(Hg)}_X(\text{l})$;
 $\text{PbCl}_2(\text{m})$; $\text{AgCl}(\text{s})$, $\text{Ag}(\text{s})$ $m_{\text{ref}} = 0.00050 \text{ mol}\cdot\text{kg}^{-1}$.
 Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\gamma/\gamma_{\text{ref}}$
.001000	.9605
.002000	.8956
.005000	.7849
.010000	.6748

Comments

All three electrochemical investigations appear to have been carefully performed and are in reasonably good agreement with one another. The results reported by Allmand and Hunter [15] appear anomalous at the lowest molalities. We have decided to give these eight data points zero weight because, if they were correct, it would indicate that γ has become substantially greater than unity at the lowest molalities. We find this difficult to accept and we prefer to believe that these difficult measurements, performed in very dilute solutions, have some systematic error(s) associated with them. The effect of the solubility of the silver-silver chloride electrode was considered but no correction was applied since the error in $\gamma/\gamma_{\text{ref}}$ is less than 0.003 at a molality of $0.0000794 \text{ mol}\cdot\text{kg}^{-1}$, which is the lowest molality for which there is experimental data. Eqs 1 could not be used for this system since too negative a value of the B coefficients is required; this, in turn, requires the taking of the logarithm of a negative number in the calculation of the osmotic coefficient. We have based the table of recommended values on the coefficients for eqs 3.



Deviation Plot For PbCl_2 : $\Delta\gamma$ vs molality

- ▲ Allmand and Hunter [15], emf measurements
- + Carmody [16], emf measurements
- × Hannan [17], emf measurements

Pb(ClO₄)₂Recommended Values for the mean activity and osmotic coefficient of Pb(ClO₄)₂ in H₂O at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8886	.9623	.999948	-1.
.002	.8510	.9494	.999897	-2.
.003	.8248	.9405	.999848	-3.
.004	.8043	.9335	.999798	-4.
.005	.7874	.9277	.999749	-6.
.006	.7729	.9227	.999701	-8.
.007	.7602	.9184	.999653	-10.
.008	.7489	.9146	.999605	-12.
.009	.7388	.9112	.999557	-14.
.010	.7295	.9081	.999509	-17.
.020	.6658	.8876	.999041	-44.
.030	.6275	.8762	.998580	-76.
.040	.6005	.8690	.998123	-113.
.050	.5801	.8641	.997668	-152.
.060	.5638	.8608	.997213	-194.
.070	.5505	.8585	.996757	-237.
.080	.5393	.8570	.996302	-282.
.090	.5298	.8561	.995845	-329.
.100	.5216	.8556	.995386	-377.
.200	.4765	.8638	.990706	-900.
.300	.4604	.8815	.985809	-1466.
.400	.4559	.9028	.980673	-2048.
.500	.4577	.9260	.975286	-2631.
.600	.4638	.9507	.969642	-3208.
.700	.4732	.9764	.963736	-3772.
.800	.4853	1.0029	.957562	-4319.
.900	.4997	1.0303	.951120	-4846.
1.000	.5163	1.0583	.944407	-5350.
1.250	.5668	1.1309	.926442	-6495.
1.500	.6302	1.2065	.906821	-7454.
1.750	.7073	1.2843	.885618	-8206.
2.000	.7995	1.3637	.862946	-8737.
2.250	.9086	1.4441	.838948	-9035.
2.500	1.0367	1.5250	.813793	-9091.
2.750	1.1862	1.6059	.787665	-8899.
3.000	1.3600	1.6865	.760758	-8454.
3.250	1.5611	1.7662	.733271	-7755.
3.500	1.7928	1.8449	.705399	-6798.
3.750	2.0586	1.9223	.677332	-5584.
4.000	2.3625	1.9980	.649249	-4113.
4.250	2.7085	2.0719	.621316	-2388.
4.500	3.1008	2.1439	.593682	-409.
4.750	3.5440	2.2138	.566480	1819.
5.000	4.0426	2.2814	.539826	4294.
5.250	4.6016	2.3468	.513816	7012.
5.500	5.2258	2.4099	.488531	9969.
5.750	5.9204	2.4707	.464034	13159.
6.000	6.6904	2.5291	.440374	16580.
6.250	7.5413	2.5853	.417584	20225.
6.500	8.4783	2.6391	.395688	24091.
6.750	9.5070	2.6908	.374695	28172.
7.000	10.6329	2.7404	.354609	32463.
7.250	11.8619	2.7878	.335422	36960.
7.500	13.1995	2.8333	.317123	41659.
7.750	14.6519	2.8769	.299694	46553.
8.000	16.2248	2.9186	.283115	51639.
8.250	17.9244	2.9585	.267360	56913.
8.500	19.7565	2.9968	.252406	62370.
8.750	21.7270	3.0335	.238224	68005.
9.000	23.8414	3.0686	.224788	73816.
9.250	26.1049	3.1021	.212070	79797.
9.500	28.5217	3.1342	.200046	85944.
9.750	31.0951	3.1647	.188689	92255.
10.000	33.8270	3.1938	.177976	98723.
10.250	36.7170	3.2212	.167884	105347.

(continued)

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	β	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
10.500	39.7624	3.2471	.158394	112120.
10.750	42.9568	3.2712	.149486	119040.
10.830(sat)	44.0089	3.2785	.146756	121284.
11.000	46.2897	3.2934	.141144	126101.
11.250	49.7453	3.3137	.133350	133298.
11.500	53.3014	3.3317	.126093	140626.
11.750	56.9285	3.3472	.119361	148080.
12.000	60.5883	3.3599	.113144	155653.
12.250	64.2330	3.3696	.107433	163339.
12.500	67.8041	3.3757	.102225	171129.
12.579	68.9064	3.3769	.100683	173611.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\sigma(\beta)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0001	.0002	.0002
.010	.0007	.0016	.0012
.100	.0023	.0065	.0034
1.000	.0017	.0093	.0048
2.000	.0022	.0084	.0067
5.000	.0018	.0090	.0364
10.000	.0018	.0086	.2897
12.579	.0045	.0094	.6491

Coefficients of Correlating Equations

Par	Eqs 1		Eqs 2		Eqs 3	
	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$
1	.1607853232+01	.407-01	.8672015468+00	.251+00	.9059790425+01	.281+00
2	.3325691636+00	.173-01	.9879588196+01	.877+00	-.1238427895+02	.983+00
3	.9833506008-01	.623-02	-.7540781480+01	.134+01	.1124508986+02	.150+01
4	-.1649240822-01	.108-02	.4910253944+01	.112+01	-.6350840933+01	.125+01
5	.1096664345-02	.864-04	-.2100887673+01	.541+00	.2261187066+01	.606+00
6	-.2798170130-04	.257-05	.5395236465+00	.153+00	-.4987439586+00	.171+00
7			-.7535352487-01	.232-01	.6250272461-01	.260-01
8			.4398133764-02	.147-02	-.3409882510-02	.165-02

$$\begin{aligned}\sigma(\text{eqs 1}) &= .463-02 \\ \sigma(\text{eqs 2}) &= .446-02 \\ \sigma(\text{eqs 3}) &= .499-02\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

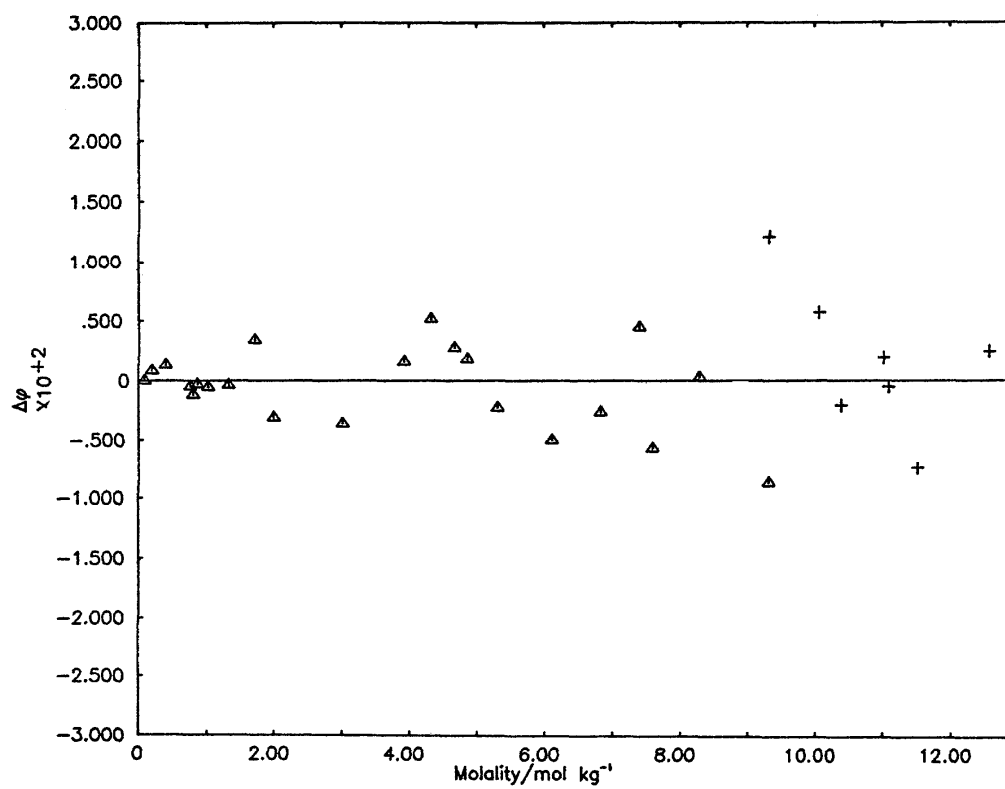
Biggs, Parton and Robinson [18]. Isopiestic measurements, reference salt is CaCl_2 . Assigned weight is 1.0.

Biggs, Parton and Robinson [18]. Isopiestic measurements, reference electrolyte is H_2SO_4 . Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\beta_{298.15}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$\beta_{298.15}$
.095290	.8558	9.324000	3.1239
.200100	.8647	10.074000	3.2078
.400800	.9043	10.397000	3.2346
.763200	.9926	11.014000	3.2966
.803000	1.0026	11.094000	3.3008
.868500	1.0213	11.520000	3.3256
1.025000	1.0649	12.579000	3.3794
1.330000	1.1545		
1.712000	1.2758		
1.999000	1.3603		
3.015000	1.6877		
3.928000	1.9780		
4.327000	2.0995		
4.675000	2.1958		
4.861000	2.2459		
5.315000	2.3612		
6.109000	2.5489		
6.827000	2.7037		
7.397000	2.8193		
7.592000	2.8439		
8.294000	2.9657		
9.304000	3.1005		

Comments

It should be noted that the data apparently extend to supersaturated solutions.



Deviation Plot for $\text{Pb}(\text{ClO}_4)_2$: $\Delta\phi$ vs molality

- ▲ Biggs, Parton and Robinson [18], isopiestic vs CaCl_2
- + Biggs, Parton and Robinson [18], isopiestic vs H_2SO_4

Pb(NO₃)₂

Recommended Values for the mean activity and osmotic coefficient of Pb(NO₃)₂ in H₂O at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8825	.9590	.999948	-1.
.002	.8398	.9431	.999898	-2.
.003	.8092	.9313	.999849	-3.
.004	.7846	.9216	.999801	-5.
.005	.7639	.9133	.999753	-7.
.006	.7459	.9059	.999706	-9.
.007	.7299	.8993	.999660	-11.
.008	.7155	.8932	.999614	-14.
.009	.7024	.8876	.999568	-16.
.010	.6903	.8824	.999523	-19.
.020	.6038	.8431	.999089	-52.
.030	.5486	.8161	.998678	-93.
.040	.5081	.7954	.998282	-141.
.050	.4764	.7785	.997898	-193.
.060	.4505	.7643	.997525	-251.
.070	.4288	.7521	.997159	-312.
.080	.4101	.7414	.996800	-376.
.090	.3938	.7319	.996446	-444.
.100	.3794	.7234	.996098	-515.
.200	.2909	.6687	.992798	-1344.
.300	.2455	.6391	.989691	-2329.
.400	.2162	.6188	.986711	-3422.
.500	.1950	.6027	.983845	-4601.
.600	.1786	.5884	.981101	-5850.
.700	.1652	.5749	.978486	-7161.
.800	.1539	.5616	.976008	-8526.
.900	.1441	.5486	.973668	-9943.
1.000	.1356	.5357	.971461	-11406.
1.250	.1182	.5057	.966415	-15252.
1.500	.1053	.4822	.961662	-19332.
1.750	.0960	.4710	.956433	-23606.
1.830 (sat)	.0938	.4710	.954489	-25008.
1.988	.0904	.4773	.950008	-27811.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0001	.0002	.0002
.010	.0007	.0016	.0011
.100	.0029	.0077	.0029
1.000	.0024	.0092	.0012
1.988	.0059	.0108	.0010

Coefficients of Correlating Equations

Par	Eqs 1		Eqs 2		Eqs 3	
	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$
1	.4873110384+00	.557-01	-.1109699871+02	.411+00	.4247477753+00	.330+00
2	.5174873883+00	.178+00	.5384915958+02	.230+01	.1546992986+02	.185+01
3	.4091921693+00	.942-01	-.8636961144+02	.529+01	-.3592544184+02	.424+01
4	.1027104527+00	.220-01	.7821019421+02	.596+01	.3633476380+02	.478+01
5			-.3624567602+02	.325+01	-.1760808369+02	.261+01
6			.6730022646+01	.689+00	.3334925159+01	.552+00

$$\sigma(\text{eqs 1}) = .736-02$$

$$\sigma(\text{eqs 2}) = .483-02$$

$$\sigma(\text{eqs 3}) = .387-02$$

Experimental Data Employed in Generation of Correlating Equations

Biggs, Parton and Robinson [18]. Isopiestic measurements, reference salt is CaCl_2 . Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.088010	.7533 *
.143700	.7148 *
.246400	.6683
.305700	.6494
.325000	.6436
.345900	.6378
.429500	.6173
.522200	.5968
.679200	.5715
.851100	.5456
.924500	.5378
1.055000	.5259
1.165000	.5112
1.279000	.5013
1.487000	.4884
1.627000	.4800
1.825000	.4733
1.988000	.4652

Hausrath [19]. Freezing point depression measurements. ϕ_i for $\text{Zn}(\text{NO}_3)_2$ and the Debye-Hückel limiting slope ($150.38 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1/2}$) for ϕ_C was used in treating these and the other freezing point depression data for this system. Assigned weight is 1.0

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.000413	1.0317 *
.000787	.9733
.001204	.9480
.001754	.9422
.002425	.8802 *
.003450	.9036
.004495	.8996
.005570	.8884
.000988	1.0161 *
.001457	.9503
.002055	.9372
.002805	.9235
.003154	1.0318 *
.004332	.8976
.005072	.8908
.000123	.9552
.000362	.9842
.000780	.9567
.001617	.9391
.003157	.9195
.005808	.8969
.009022	.8759
.017370	.8379

Motornaya et al. [20]. Isopiestic measurements, reference salt is CaCl_2 . Assigned weight is 0.30.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
1.160000	.5082
1.329000	.4967
1.520000	.4866
1.652000	.4819
1.758000	.4771
1.160000	.5082
1.318000	.4827 *
1.575000	.4838
1.650000	.4800
1.758000	.4783

Motornaya and Ben'yash [21]. Isopiestic measurements, reference salt was not specified by authors. Assigned weight is 0.30.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.200000	.6920
.400000	.6280
.600000	.5880
.800000	.5580
1.000000	.5330
1.200000	.5110
1.400000	.4940
1.600000	.4810
1.758000	.4770

Plake [22]. Freezing point depression measurements. Assigned weight is zero.

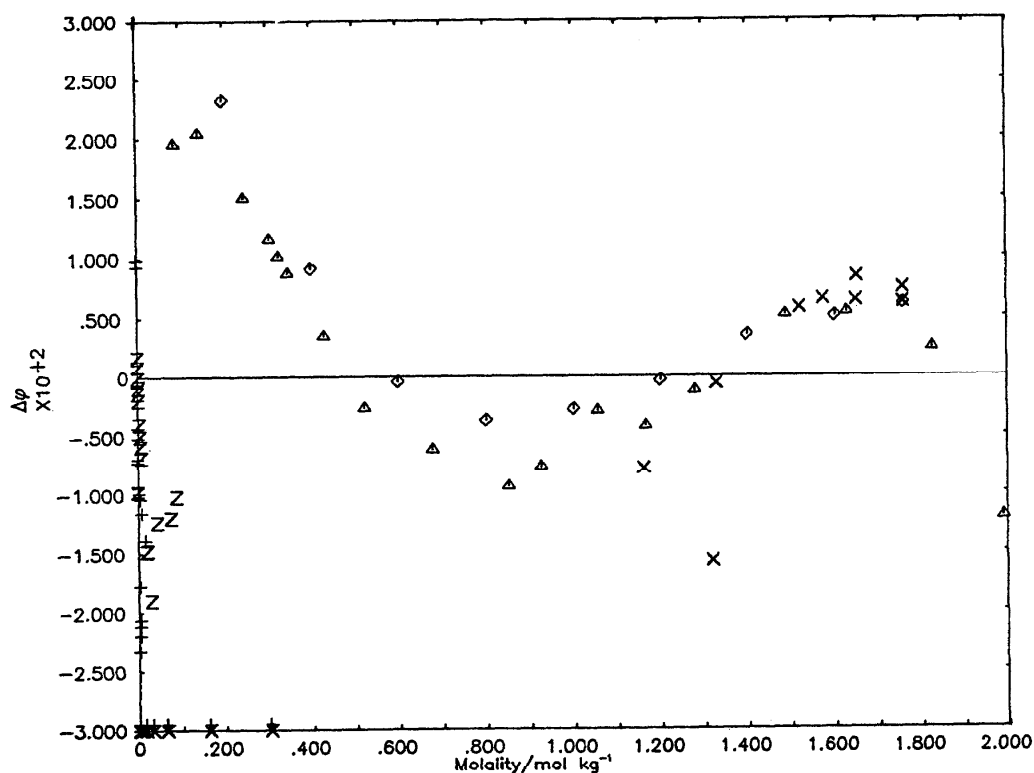
$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.000809	.2822
.001620	.2703
.003240	.2571
.006470	.2447
.015800	.2316
.032700	.2197
.065000	.2117
.163000	.2057
.303000	.1992

Randall and Vaneslow [23]. Freezing point depression measurements. Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.000960	.9500
.001400	.9518
.002090	.9428
.002880	.9306
.004390	.9174
.006500	.8975
.009130	.8801
.030800	.7953
.076200	.7333
.000940	.9619
.001840	.9439
.004290	.9161
.007340	.8913
.022670	.8203
.020170	.8277
.044350	.7753
.089670	.7220

Comments

The isopiestic data of Biggs et al, [18] merge very nicely with the freezing point depression data of Randall and Vaneslow [23] once the data for the lowest two molalities of the former data set have been discarded. The more recent isopiestic data of Motornaya et al [20] and of Motornaya and Ben'yash [21] are also in reasonable agreement with the results of Biggs et al [18]. Conrad [24] reports data for a concentration cell with transference utilizing lead-mercury amalgam electrodes. However, in the absence of transference numbers, this data set cannot be treated. The freezing point depression measurements of Plake [22] are totally unreasonable and were given zero weight. Plake's [22] boiling point elevation data and Ratner's [25] vapor pressure data at 70°C were not created since the temperature corrections to 25°C are large and uncertain. One data point of Biggs et al. [18] apparently refers to a supersaturated solution.



Deviation Plot for $Pb(NO_3)_2$: $\Delta\phi$ vs molality

- Δ Biggs, Parton, and Robinson [18], isopiestic vs $CaCl_2$
- + Hausrath [19], freezing point depression
- X Motornaya et al. [20], isopiestic vs $CaCl_2$
- \diamond Motornaya and Ben'yash [21], isopiestic vs ?
- X Plake [22], freezing point depression
- Z Randall and Vaneslow [23], freezing point depression

CuCl₂Recommended Values for the mean activity and osmotic coefficient of CuCl₂ in H₂O at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8873	.9616	.999948	-1.
.002	.8487	.9481	.999898	-2.
.003	.8216	.9386	.999848	-3.
.004	.8003	.9311	.999799	-5.
.005	.7826	.9248	.999750	-6.
.006	.7674	.9195	.999702	-8.
.007	.7541	.9147	.999654	-10.
.008	.7423	.9105	.999606	-12.
.009	.7315	.9067	.999559	-15.
.010	.7217	.9033	.999512	-17.
.020	.6538	.8796	.999050	-45.
.030	.6124	.8659	.998597	-79.
.040	.5831	.8567	.998150	-118.
.050	.5606	.8501	.997705	-159.
.060	.5427	.8453	.997263	-204.
.070	.5278	.8417	.996821	-250.
.080	.5153	.8390	.996379	-299.
.090	.5046	.8370	.995937	-349.
.100	.4952	.8356	.995494	-400.
.200	.4415	.8358	.991006	-972.
.300	.4183	.8466	.986368	-1602.
.400	.4066	.8605	.981570	-2262.
.500	.4007	.8754	.976622	-2937.
.600	.3982	.8906	.971534	-3620.
.700	.3980	.9056	.966319	-4305.
.800	.3992	.9203	.960989	-4990.
.900	.4015	.9346	.955556	-5670.
1.000	.4046	.9485	.950030	-6346.
1.250	.4146	.9810	.935877	-8007.
1.500	.4266	1.0103	.921357	-9617.
1.750	.4397	1.0368	.906596	-11173.
2.000	.4531	1.0604	.891700	-12673.
2.250	.4667	1.0816	.876757	-14117.
2.500	.4802	1.1004	.861838	-15507.
2.750	.4934	1.1173	.846998	-16846.
3.000	.5063	1.1323	.832279	-18135.
3.250	.5189	1.1457	.817709	-19377.
3.500	.5312	1.1579	.803303	-20575.
3.750	.5432	1.1689	.789069	-21730.
4.000	.5549	1.1790	.775000	-22845.
4.250	.5665	1.1886	.761084	-23921.
4.500	.5781	1.1977	.747298	-24958.
4.750	.5897	1.2067	.733614	-25959.
5.000	.6015	1.2157	.719996	-26923.
5.250	.6136	1.2249	.706404	-27849.
5.500	.6263	1.2347	.692790	-28738.
5.750	.6397	1.2452	.679104	-29588.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0000	.0001	.0001
.010	.0002	.0005	.0004
.100	.0009	.0024	.0012
1.000	.0007	.0035	.0014
2.000	.0009	.0032	.0015
5.000	.0017	.0042	.0025
5.750	.0033	.0045	.0029

Coefficients of Correlating Equations

Par	Eqs 1		Eqs 2		Eqs 3	
	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$
1	.1364012482+02	.131-01	.3850362139+00	.207+00	.1070227413+02	.440+00
2	.3521422676+00	.744-02	.1062009149+02	.852+00	-.2257992723+02	.221+01
3	-.4836702212-01	.242-02	-.8247488997+01	.149+01	.3436092748+02	.488+01
4	.3122205079-02	.258-03	.5160485129+01	.138+01	-.3405642618+02	.590+01
5			-.2093950846+01	.700+00	.2132204383+02	.419+01
6			.4792176667+00	.185+00	-.8118651681+01	.174+01
7			-.4645811863-01	.198-01	.1712850567+01	.389+00
8					-.1532701426+00	.364-01

$$\sigma(\text{eqs 1}) = .425-02$$

$$\sigma(\text{eqs 2}) = .369-02$$

$$\sigma(\text{eqs 3}) = .370-02$$

Experimental Data Employed in Generation of Correlating Equations

Downes and Pitzer [26]. Isopiestic measurements, reference salt is CaCl_2 . Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.187500	.8367
.239800	.8383
.315400	.8474
.361000	.8522
.443100	.8644
.519900	.8744
.692000	.8998
.835200	.9190
.852700	.9235
1.027800	.9487
1.168400	.9691
1.370300	.9923
1.599500	1.0215
1.838100	1.0455
2.248200	1.0755

Downes and Pitzer [26]. Isopiestic measurements, reference salt is NaCl . Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.225400	.8397
.275000	.8441
.358400	.8523
.373100	.8552
.505100	.8721
.633400	.8914
.682300	.9005
.815600	.9188
.876300	.9274
.883200	.9269
1.015500	.9479
1.081700	.9557
1.287900	.9844
1.309800	.9874
1.379700	.9946
1.565800	1.0175
1.684600	1.0280
1.901900	1.0498
1.939700	1.06451

Huang and Pan [27]. Freezing point depression measurements. The ϕ_L and ϕ_C data for $\text{Cu}(\text{ClO}_4)_2$ given in the table of auxiliary data were used in treating these and the other freezing point depression measurements. Assigned weight is zero.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.002500	.9803
.003500	.9709
.005300	.9243
.007400	.8986
.009600	.8881
.015200	.8690
.017400	.8587
.022000	.8450
.028500	.8331
.033800	.8211
.041400	.8006
.048900	.7969
.049500	.7956
.068500	.7646
.076500	.7554
.098000	.7622

Jones and Getman [28]. Freezing point depression measurements. Assigned weight is zero.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.065050	.9112
.130300	.8804
.261000	.8798

Jones and Pearce [29]. Freezing point depression measurements. Assigned weight is zero.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.010000	1.0195
.050030	.8923
.075070	.8847
.100100	.8718
.250800	.8798

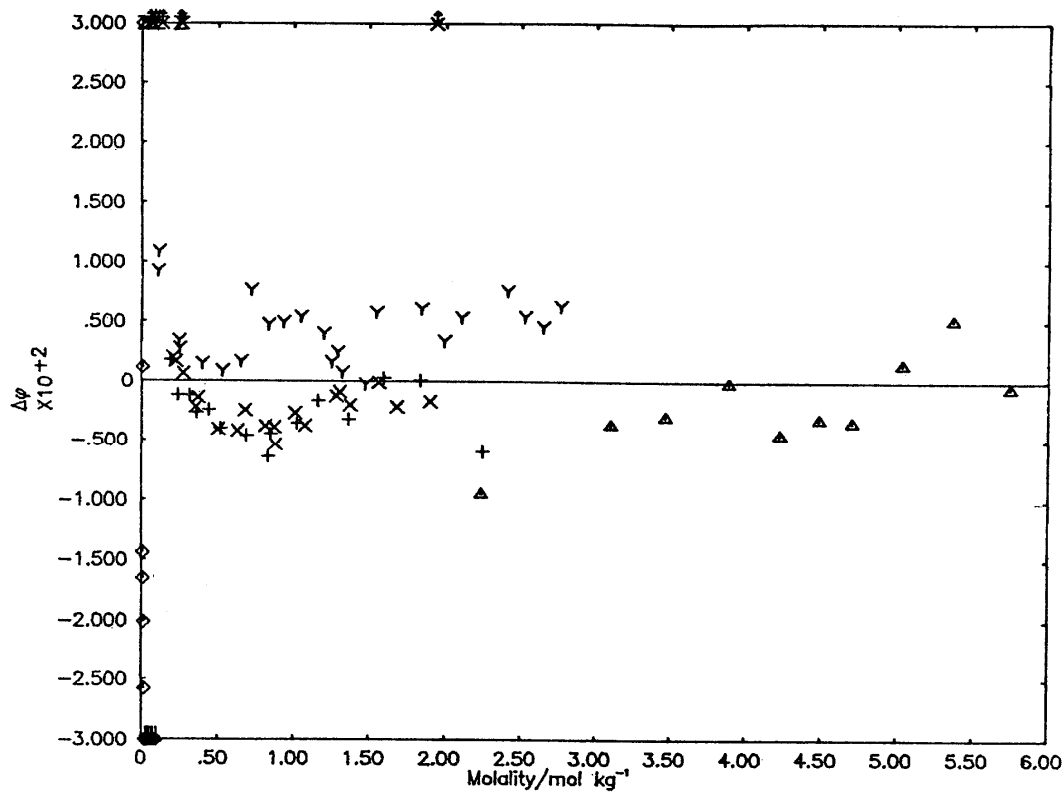
Robinson and Stokes [30]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

Brown [39]. Isopiestic measurements, reference salt is CaCl_2 . Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.108500	.8439	2.236000	1.0710
.112800	.8452	3.100000	1.1342
.204800	.8382	3.466000	1.1533
.247400	.8437	3.887000	1.1744
.251600	.8435	4.226000	1.1832
.359800	.8619	4.482000	1.1939
.533400	.8813	4.701000	1.2015
.655500	.9006	5.033000	1.2183
.723600	.9168	5.367000	1.2346
.838800	.9307	5.750000	1.2447
.937800	.9449		
1.054000	.9612		
1.206000	.9795		
1.259000	.9837		
1.297000	.9892		
1.328000	.9912		
1.481000	1.0080		
1.553000	1.0220		
1.847000	1.0524		
1.996000	1.0635		
2.111000	1.0755		
2.415000	1.1019		
2.530000	1.1080		
2.652000	1.1155		
2.769000	1.1248		

Comments

The isopiestic data of Downes and Pitzer [26] are in good agreement with the earlier results of Robinson and Stokes [30] and Brown [39]. The freezing point depression data do not appear to be very accurate. If the solubility tabulated by Linke and Seidell [9] is correct, one data point of Brown's [39] refers to a supersaturated solution.



Deviation Plot for CuCl_2 : $\Delta\theta$ vs molality

- △ Brown [39], Isopiestic vs CaCl_2
- + Downes and Pitzer [26], isopiestic vs CaCl_2
- × Downes and Pitzer [26], isopiestic vs NaCl
- ◇ Huang and Pan [27], freezing point depression
- ⊗ Jones and Getman [28], freezing point depression
- Z Jones and Pearce [29], freezing point depression
- Y Robinson and Stokes [30], Isopiestic vs KCl .

Cu(ClO₄)₂Recommended Values for the mean activity and osmotic coefficient of Cu(ClO₄)₂ in H₂O at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8905	.9634	.999948	-1.
.002	.8545	.9514	.999897	-2.
.003	.8296	.9432	.999847	-3.
.004	.8104	.9370	.999797	-4.
.005	.7946	.9319	.999748	-6.
.006	.7812	.9277	.999699	-8.
.007	.7695	.9241	.999650	-10.
.008	.7592	.9209	.999602	-12.
.009	.7499	.9181	.999554	-14.
.010	.7415	.9156	.999505	-16.
.020	.6849	.9002	.999027	-41.
.030	.6521	.8931	.998553	-72.
.040	.6298	.8896	.998079	-105.
.050	.6135	.8881	.997603	-140.
.060	.6010	.8880	.997125	-177.
.070	.5911	.8887	.996644	-216.
.080	.5832	.8900	.996159	-255.
.090	.5768	.8918	.995671	-296.
.100	.5716	.8940	.995180	-337.
.200	.5534	.9260	.990041	-770.
.300	.5629	.9657	.984464	-1206.
.400	.5854	1.0089	.978426	-1619.
.500	.6168	1.0544	.971908	-1999.
.600	.6561	1.1020	.964896	-2336.
.700	.7028	1.1514	.957375	-2624.
.800	.7573	1.2025	.949337	-2859.
.900	.8200	1.2552	.940773	-3036.
1.000	.8916	1.3094	.931678	-3153.
1.250	1.1179	1.4513	.906607	-3159.
1.500	1.4290	1.6014	.878253	-2726.
1.750	1.8563	1.7586	.846768	-1822.
2.000	2.4446	1.9220	.812411	-418.
2.250	3.2563	2.0904	.775535	1509.
2.500	4.3791	2.2629	.736571	3978.
2.750	5.9346	2.4383	.696009	7005.
3.000	8.0913	2.6155	.654374	10603.
3.250	11.0798	2.7935	.612209	14782.
3.500	15.2137	2.9712	.570050	19548.
3.557	16.3558	3.0114	.560509	20716.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0003	.0005	.0005
.010	.0016	.0036	.0026
.100	.0043	.0131	.0075
1.000	.0029	.0158	.0140
2.000	.0030	.0152	.0373
3.557	.0055	.0157	.2561

Coefficients of Correlating Equations

Par	Eqs 1		Eqs 2		Eqs 3	
	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$
1	.1919717293+01	.984-01	.2257716470+01	.322+00	.9636429133+01	.390+00
2	.6710180343+00	.392-01	.6937781666+01	.894+00	-.1153564422+02	.108+01
3	.1724723689+00	.180-01	-.3137567384+01	.971+00	.8393756854+01	.118+01
4	-.1593987363-01	.278-02	.1156592753+01	.469+00	-.3000756643+01	.568+00
5			-.1927565769+00	.843-01	.4210928109+00	.102+00

$$\begin{aligned}\sigma(\text{eqs } 1) &= .600-02 \\ \sigma(\text{eqs } 2) &= .626-02 \\ \sigma(\text{eqs } 3) &= .757-02\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Libus and Sadowska [31],
isopiestic measurements, ref-
erence salt is KCl. Assigned
weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\delta_{298.15}$
.111100	.8926
.374400	1.0019
.657900	1.1302
.808600	1.2076
1.032800	1.3258
1.387500	1.5330
1.690100	1.7283

Libus and Sadowska [31],
isopiestic measurements, ref-
erence salt is $\text{Mg}(\text{ClO}_4)_2$.
Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\delta_{298.15}$
2.847100	2.5138
3.190300	2.7545
3.666900	3.0085

Libus and Sadowska [31],
isopiestic measurements, ref-
erence salt is NaClO_4 . Assigned
weight is 1.0.

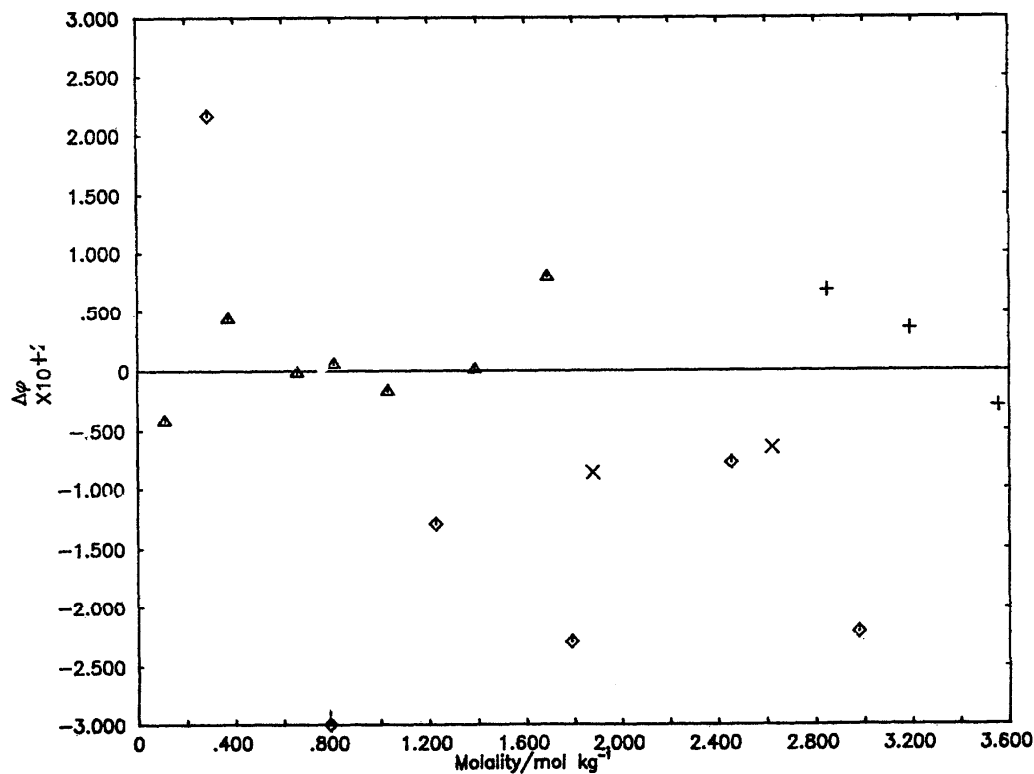
$m/\text{mol}\cdot\text{kg}^{-1}$	$\delta_{298.15}$
1.879200	1.8337
2.622900	2.3423

Lilich and Andreev [32].
Vapor pressure measurements.
Assigned weight is zero.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\delta_{298.15}$
.292000	.9840
.790000	1.1402
1.228000	1.4255
1.788000	1.7601
2.456000	2.2245
2.975000	2.5756

Comments

We prefer the isopiestic measurements of Libus and Sadowska [31] over the less precise vapor pressure measurements of Lilich and Andreev [32].



Deviation Plot for $\text{Cu}(\text{ClO}_4)_2$: $\Delta\delta$ vs molality

▲ Libus and Sadowska [31], isopiestic vs KCl

× Libus and Sadowska [31], isopiestic vs NaClO_4

+ Libus and Sadowska [31], isopiestic vs $\text{Mg}(\text{ClO}_4)_2$

◇ Lilich and Andreev [32], vapor pressure

CuBr₂Recommended Values for the mean activity and osmotic coefficient of CuBr₂ in H₂O at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8895	.9628	.999948	-1.
.002	.8526	.9504	.999897	-2.
.003	.8271	.9418	.999847	-3.
.004	.8071	.9351	.999798	-4.
.005	.7907	.9296	.999749	-6.
.006	.7767	.9250	.999700	-8.
.007	.7645	.9210	.999652	-10.
.008	.7536	.9175	.999603	-12.
.009	.7439	.9144	.999555	-14.
.010	.7350	.9115	.999507	-16.
.020	.6743	.8931	.999035	-43.
.030	.6382	.8834	.998569	-74.
.040	.6130	.8776	.998105	-109.
.050	.5941	.8739	.997641	-147.
.060	.5791	.8717	.997177	-186.
.070	.5670	.8704	.996713	-228.
.080	.5569	.8698	.996247	-271.
.090	.5484	.8697	.995779	-315.
.100	.5411	.8700	.995309	-360.
.200	.5036	.8846	.990483	-849.
.300	.4938	.9076	.985391	-1368.
.400	.4953	.9338	.980016	-1893.
.500	.5033	.9614	.974354	-2410.
.600	.5155	.9900	.968408	-2912.
.700	.5309	1.0189	.962187	-3394.
.800	.5490	1.0479	.955705	-3853.
.900	.5691	1.0766	.948979	-4285.
1.000	.5911	1.1049	.942030	-4691.
1.250	.6522	1.1725	.923845	-5577.
1.500	.7193	1.2335	.904840	-6280.
1.750	.7892	1.2862	.885461	-6806.
2.000	.8588	1.3296	.866130	-7166.
2.250	.9256	1.3636	.847196	-7378.
2.500	.9877	1.3889	.828899	-7459.
2.750	1.0444	1.4067	.811338	-7429.
3.000	1.0963	1.4193	.794441	-7303.
3.250	1.1459	1.4295	.777944	-7090.
3.500	1.1974	1.4413	.761369	-6796.
3.606	1.2213	1.4478	.754154	-6647.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0001	.0002	.0002
.010	.0007	.0016	.0012
.100	.0017	.0055	.0030
1.000	.0012	.0050	.0030
2.000	.0015	.0060	.0052
3.606	.0034	.0068	.0083

Coefficients of Correlating Equations

Par	Eqs 1		Eqs 2		Eqs 3	
	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$
1	.1775303405+01	.479-01	.2126673350+01	.101+00	.1227403314+02	.745+00
2	.3741179583+00	.369-01	.5879036806+01	.303+00	-.2643669481+02	.365+01
3	.1768554544+00	.295-01	-.1403529095+01	.347+00	.3873508789+02	.766+01
4	-.8733461380-01	.104-01	-.3840632784-01	.175+00	-.3484168111+02	.850+01
5	.1051330459-01	.128-02	.6412463170-01	.322-01	.1857684759+02	.521+01
6					-.5413754938+01	.167+01
7					.6644180084+00	.218+00

$$\sigma(\text{eqs 1}) = .390-02$$

$$\sigma(\text{eqs 2}) = .376-02$$

$$\sigma(\text{eqs 3}) = .377-02$$

Experimental Data Employed in Generation of Correlating Equations

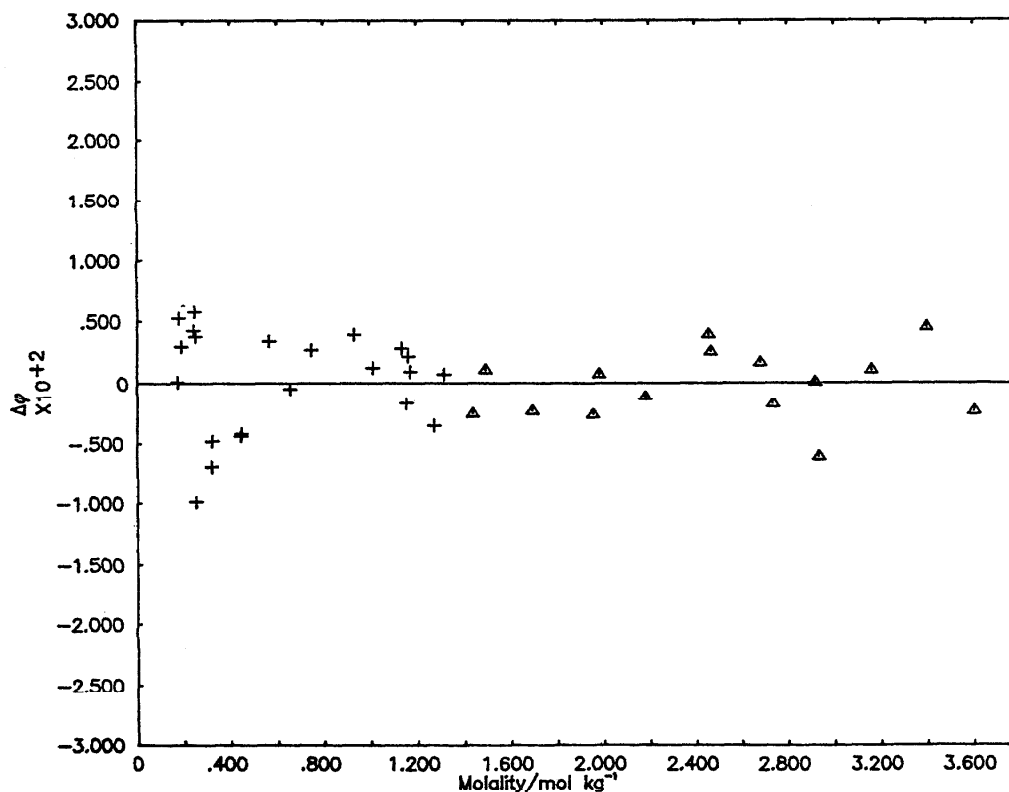
Libus et al. [32a,b]. Isopiestic measurements.
Reference salt is $\text{Mg}(\text{ClO}_4)_2$. Assigned weight is 1.0.

Libus et al. [32a,b]. Isopiestic measurements.
Reference salt is KCl. Assigned weight is 1.0.

$m_{\text{ref}}/\text{mol}\cdot\text{kg}^{-1}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$	$m_{\text{ref}}/\text{mol}\cdot\text{kg}^{-1}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
1.213	1.438000	1.2165	0.2556	.176000	.8801
1.256	1.495000	1.2334	0.2633	.180000	.8860
1.391	1.695000	1.2730	0.2804	.191500	.8859
1.558	1.956000	1.3200	0.3626	.243200	.8983
1.578	1.985000	1.3280	0.3687	.246600	.9006
1.692	2.181000	1.3540	0.3761	.251700	.8998
1.847	2.459000	1.3892	0.3743	.254200	.8867
1.851	2.469000	1.3887	0.4879	.323000	.9066
1.958	2.685000	1.4043	0.4905	.323900	.9089
1.980	2.737000	1.4041	0.704	.447200	.9423
2.066	2.920000	1.4157	0.706	.448200	.9428
2.068	2.936000	1.4103	0.934	.568000	.9842
2.174	3.164000	1.4271	1.101	.656000	1.0057
2.277	3.399000	1.4406	1.290	.748000	1.0355
2.359	3.606000	1.4454	1.681	.932000	1.0897
			1.859	1.015000	1.1104
			2.133	1.136000	1.1452
			2.168	1.155000	1.1458
			2.200	1.166000	1.1526
			2.216	1.174000	1.1535
			2.439	1.275000	1.1754
			2.549	1.319000	1.1908

Comments

The data for this system are based on the isopiestic measurement of Libus et al. [32a]. It should be noted that, in their data tables, there exists an erroneous setting of the columns for the data for NiBr_2 and CuBr_2 . The correct [32b] experimental data for this system is given above along with the calculated osmotic coefficients.



Deviation Plot for CuBr_2 : $\Delta\phi$ vs molality

▲ Libus et al. [32a,b], isopiestic vs $\text{Mg}(\text{ClO}_4)_2$

+ Libus et al. [32a,b], isopiestic vs KCl

$\text{Cu}(\text{NO}_3)_2$ Recommended Values for the mean activity and osmotic coefficient of $\text{Cu}(\text{NO}_3)_2$ in H_2O at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8885	.9623	.999948	-1.
.002	.8508	.9493	.999897	-2.
.003	.8245	.9403	.999848	-3.
.004	.8039	.9332	.999798	-5.
.005	.7869	.9274	.999749	-6.
.006	.7724	.9224	.999701	-8.
.007	.7596	.9180	.999653	-10.
.008	.7483	.9142	.999605	-12.
.009	.7380	.9107	.999557	-14.
.010	.7287	.9076	.999510	-17.
.020	.6643	.8865	.999042	-44.
.030	.6254	.8745	.998583	-77.
.040	.5978	.8667	.998128	-113.
.050	.5768	.8613	.997675	-153.
.060	.5600	.8574	.997224	-195.
.070	.5461	.8545	.996772	-239.
.080	.5344	.8524	.996321	-285.
.090	.5244	.8509	.995870	-332.
.100	.5156	.8499	.995417	-381.
.200	.4656	.8521	.990831	-917.
.300	.4445	.8637	.986094	-1505.
.400	.4347	.8787	.981183	-2117.
.500	.4311	.8955	.976091	-2740.
.600	.4314	.9136	.970808	-3366.
.700	.4344	.9326	.965331	-3989.
.800	.4397	.9525	.959654	-4605.
.900	.4469	.9730	.953775	-5210.
1.000	.4556	.9941	.947690	-5802.
1.250	.4836	1.0492	.931570	-7211.
1.500	.5197	1.1071	.914158	-8496.
1.750	.5636	1.1671	.895488	-9639.
2.000	.6154	1.2287	.875624	-10624.
2.250	.6756	1.2915	.854659	-11441.
2.500	.7447	1.3549	.832709	-12080.
2.750	.8234	1.4186	.809906	-12535.
3.000	.9123	1.4820	.786395	-12801.
3.250	1.0124	1.5450	.762328	-12875.
3.500	1.1242	1.6071	.737860	-12755.
3.750	1.2485	1.6680	.713146	-12440.
4.000	1.3862	1.7276	.688333	-11930.
4.250	1.5378	1.7855	.663561	-11226.
4.500	1.7041	1.8417	.638959	-10330.
4.750	1.8855	1.8959	.614641	-9245.
5.000	2.0827	1.9481	.590708	-7973.
5.250	2.2961	1.9982	.567247	-6518.
5.500	2.5261	2.0461	.544326	-4884.
5.750	2.7732	2.0919	.522000	-3074.
6.000	3.0378	2.1356	.500307	-1092.
6.250	3.3204	2.1774	.479271	1056.
6.500	3.6217	2.2172	.458902	3369.
6.750	3.9423	2.2554	.439197	5840.
7.000	4.2836	2.2921	.420143	8468.
7.250	4.6468	2.3275	.401715	11249.
7.500	5.0341	2.3620	.383878	14180.
7.750	5.4480	2.3958	.366593	17258.
7.840	5.6041	2.4079	.360496	18402.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0001	.0003	.0003
.010	.0009	.0021	.0015
.100	.0030	.0086	.0044
1.000	.0028	.0121	.0055
2.000	.0028	.0115	.0071
5.000	.0035	.0132	.0274
7.840	.0085	.0152	.0851

Coefficients of Correlating Equations

Par	Eqs 1		Eqs 2		Eqs 3	
	coefficient	σ (coeff)	coefficient	σ (coeff)	coefficient	σ (coeff)
1	.1607993894+01	.546-01	.3812081536-01	.414+00	.8042229122+01	.214+00
2	.2195645965+00	.283-01	.1246098401+02	.153+01	-.9152204978+01	.614+00
3	.8217691776-01	.121-01	-.1122758218+02	.236+01	.6377416305+01	.711+00
4	-.1186534502-01	.214-02	.7451806097+01	.190+01	-.2472027188+01	.403+00
5	.5202686124-03	.127-03	-.2927487178+01	.830+00	.4954651209+00	.111+00
6			.6091903704+00	.188+00	-.4028506698-01	.118-01
7			-.5182683817-01	.172-01		
8						

$$\sigma(\text{eqs 1}) = .867-02$$

$$\sigma(\text{eqs 2}) = .770-02$$

$$\sigma(\text{eqs 3}) = .387-02$$

Experimental Data Employed in Generation of Correlating Equations

Jones and Getman [28]. Freezing point depression measurements. Φ_L and Φ_C data for $\text{Cu}(\text{ClO}_4)_2$ were used in treating these and the other freezing point depression measurements. Assigned weight is zero.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\Phi_{298.15}$
.059200	.9860
.118700	.8995
.238200	.9154
.480700	.9592

Yakimov and Guzhavina [34]. Vapor pressure measurements. Assigned weight is zero.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\Phi_{298.15}$
3.723000	2.3057
3.431000	2.1587
3.106000	1.9906
2.821000	1.8601
2.496000	1.6876
2.157000	1.5363
1.714000	1.3302
1.200000	1.1752

Jones and Pearce [29]. Freezing point depression measurements. Assigned weight is zero.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\Phi_{298.15}$
.010000	1.0256
.025000	.9909
.050100	.9123
.075300	.8797
.251900	.8741
.508100	.9241

Brown [39]. Isopiestic measurements, reference salt is H_2SO_4 . Assigned weight is 1.0.

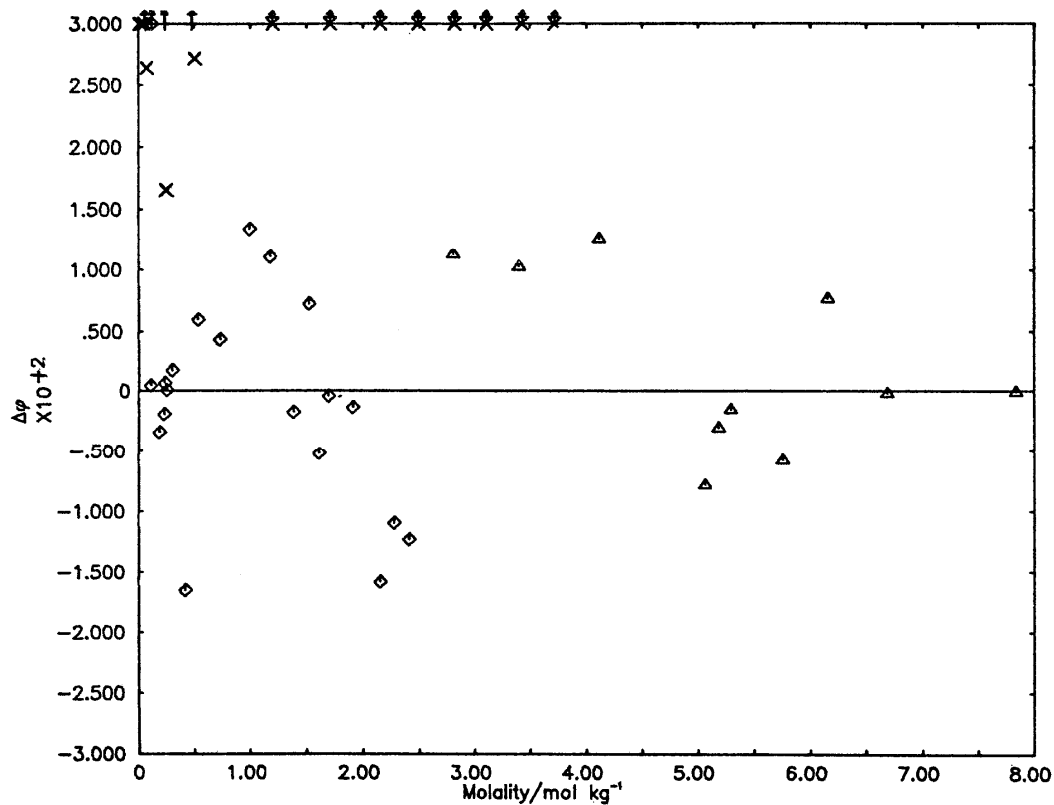
$m/\text{mol}\cdot\text{kg}^{-1}$	$\Phi_{298.15}$
2.809000	1.4448
3.400000	1.5926
4.116000	1.7673
5.067000	1.9539
5.187000	1.9827
5.295000	2.0054
5.756000	2.0872
6.160000	2.1702
6.690000	2.2462
7.840000	2.4078

Robinson, Wilson, and Ayling [33]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\Phi_{298.15}$
.109100	.8497
.121100	.9167
.192100	.8481
.233300	.8535
.238200	.8566
.258500	.8584
.306000	.8662
.424100	.8661
.538900	.9084
.731000	.9431
1.000000	1.0075
1.183000	1.0452
1.390000	1.0796
1.529000	1.1212
1.618000	1.1300
1.701000	1.1548
1.915000	1.2063
2.158000	1.2525
2.283000	1.2889
2.415000	1.3210

Comments

Both the freezing point depression measurements [28,29] and the vapor pressure data [34] have a low accuracy and precision in comparison to the isopiestic data [33,39].



Deviation Plot for $\text{Cu}(\text{NO}_3)_2$: $\Delta\phi$ vs molality

- ▲ Brown [39], isopiestic vs H_2SO_4
- + Jones and Getman [28], freezing point depression
- × Jones and Pearce [29], freezing point depression
- ◇ Robinson, Wilson, and Ayling [33], isopiestic vs KCl
- * Yakimov and Guzhavina [34], vapor pressure

Cu (C₇ H₇ O₃ S)₂

Recommended Values for the mean activity and osmotic coefficient of Cu(C₇H₇O₃S)₂, copper
p-toluene sulfonate, in H₂O at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8883	.9622	.999948	-1.
.002	.8504	.9491	.999897	-2.
.003	.8240	.9400	.999848	-3.
.004	.8032	.9327	.999798	-5.
.005	.7860	.9268	.999750	-6.
.006	.7712	.9216	.999701	-8.
.007	.7583	.9171	.999653	-10.
.008	.7467	.9131	.999605	-12.
.009	.7363	.9095	.999558	-14.
.010	.7268	.9062	.999510	-17.
.020	.6604	.8833	.999046	-44.
.030	.6195	.8695	.998591	-78.
.040	.5900	.8597	.998143	-115.
.050	.5671	.8522	.997700	-156.
.060	.5484	.8462	.997260	-199.
.070	.5327	.8412	.996823	-245.
.080	.5192	.8370	.996388	-293.
.090	.5073	.8333	.995955	-343.
.100	.4968	.8300	.995524	-394.
.200	.4292	.8090	.991293	-974.
.300	.3910	.7959	.987179	-1639.
.400	.3642	.7850	.983172	-2365.
.500	.3433	.7751	.979273	-3139.
.600	.3261	.7654	.975484	-3953.
.700	.3113	.7559	.971807	-4804.
.800	.2983	.7464	.968241	-5688.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0001	.0001	.0001
.010	.0004	.0010	.0007
.100	.0014	.0040	.0020
.800	.0020	.0047	.0014

Coefficients of Correlating Equations

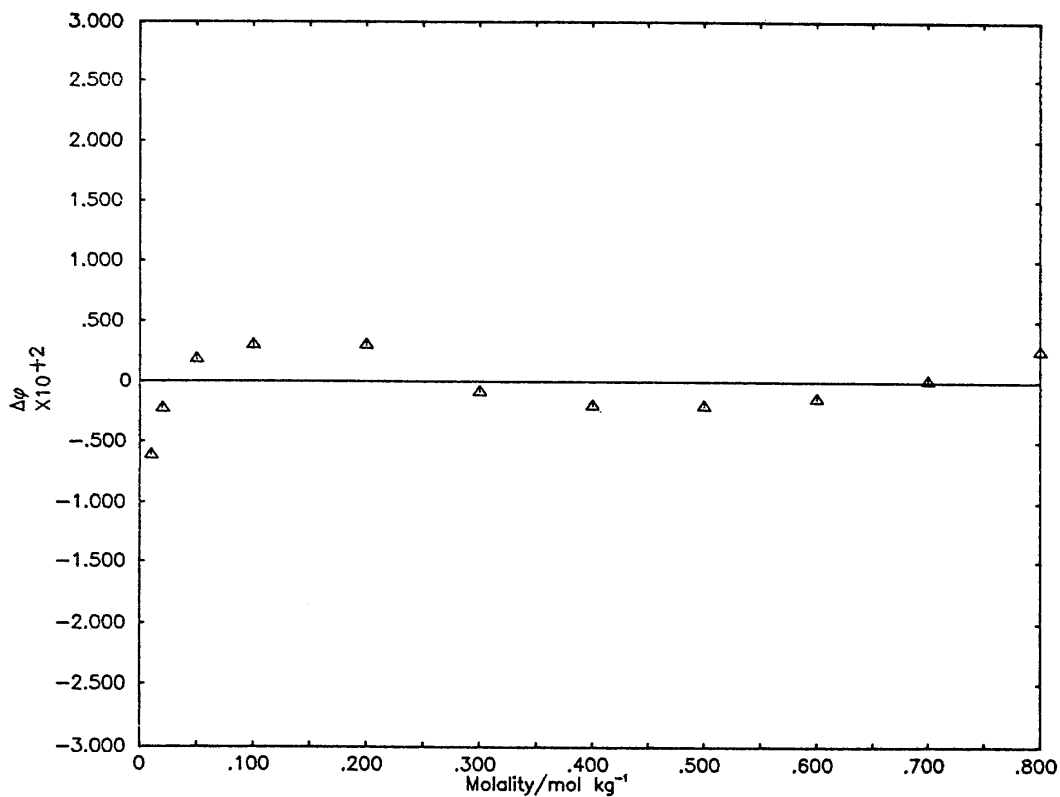
Par	Eqs 1		Eqs 2		Eqs 3	
	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$
1	.1652214843+01	.259-01	-.3010451073+00	.499+00	.9564074344+01	.148+00
2	-.2321814144+00	.111-01	.1229106397+02	.204+01	-.1535097603+02	.606+00
3			-.9958029441+01	.291+01	.1279512791+02	.866+00
4			.3865476259+01	.139+01	-.4233283559+01	.414+00

$$\begin{aligned}\sigma(\text{eqs } 1) &= .302-02 \\ \sigma(\text{eqs } 2) &= .564-02 \\ \sigma(\text{eqs } 3) &= .168-02\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Bonner, Breazeale and Rushing [35]. Vapor pressure osmometry and isopiestic measurements. The authors do not report the isopiestic molalities. Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.010000	.9000
.020000	.8810
.050000	.8540
.100000	.8330
.200000	.8120
.300000	.7950
.400000	.7830
.500000	.7730
.600000	.7640
.700000	.7560
.800000	.7490



Deviation Plot for $\text{Cu}(\text{C}_{77}\text{H}_{73}\text{O}_3\text{S})_2$: $\Delta\phi$ vs molality

▲ Bonner, Breazeale, and Rushing [35], vapor pressure osmometry and isopiestic measurements

MnCl₂Recommended Values for the mean activity and osmotic coefficient of MnCl₂ in H₂O at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8882	.9621	.999948	-1.
.002	.8503	.9491	.999897	-2.
.003	.8238	.9399	.999848	-3.
.004	.8031	.9327	.999798	-5.
.005	.7859	.9268	.999750	-6.
.006	.7712	.9217	.999701	-8.
.007	.7583	.9173	.999653	-10.
.008	.7469	.9134	.999605	-12.
.009	.7365	.9098	.999558	-14.
.010	.7271	.9066	.999510	-17.
.020	.6620	.8851	.999044	-44.
.030	.6227	.8729	.998586	-77.
.040	.5949	.8649	.998132	-114.
.050	.5737	.8595	.997680	-154.
.060	.5568	.8556	.997229	-197.
.070	.5430	.8528	.996779	-241.
.080	.5313	.8509	.996328	-288.
.090	.5213	.8495	.995876	-335.
.100	.5126	.8487	.995424	-384.
.200	.4641	.8537	.990815	-924.
.300	.4452	.8668	.986012	-1512.
.400	.4380	.8877	.980992	-2121.
.500	.4372	.9086	.975745	-2737.
.600	.4404	.9307	.970270	-3350.
.700	.4466	.9536	.964565	-3955.
.800	.4551	.9771	.958633	-4547.
.900	.4655	1.0010	.952477	-5125.
1.000	.4775	1.0251	.946106	-5684.
1.250	.5135	1.0656	.929282	-6993.
1.500	.5567	1.1456	.911309	-8158.
1.750	.6062	1.2039	.892378	-9168.
2.000	.6611	1.2597	.872696	-10018.
2.250	.7209	1.3125	.852475	-10707.
2.500	.7847	1.3619	.831922	-11236.
2.750	.8521	1.4076	.811224	-11610.
3.000	.9224	1.4496	.790545	-11833.
3.250	.9950	1.4878	.770023	-11912.
3.500	1.0694	1.5225	.749763	-11854.
3.750	1.1452	1.5538	.729846	-11665.
4.000	1.2221	1.5822	.710319	-11352.
4.250	1.2999	1.6078	.691210	-10921.
4.500	1.3786	1.6312	.672520	-10378.
4.750	1.4584	1.6527	.654236	-9729.
5.000	1.5393	1.6728	.636333	-8977.
5.250	1.6219	1.6917	.618779	-8126.
5.500	1.7063	1.7099	.601540	-7180.
5.750	1.7931	1.7275	.584587	-6140.
6.000	1.8824	1.7448	.567902	-5009.
6.250	1.9746	1.7619	.551481	-3788.
6.500	2.0697	1.7787	.535343	-2479.
6.750	2.1671	1.7950	.519530	-1084.
7.000	2.2661	1.8105	.504116	395.
7.250	2.3654	1.8247	.489209	1957.
7.500	2.4627	1.8368	.474955	3595.
7.699	2.5366	1.8444	.464199	4951.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0001	.0001	.0001
.010	.0004	.0009	.0007
.100	.0012	.0036	.0018
1.000	.0008	.0044	.0021
2.000	.0007	.0043	.0028
5.000	.0013	.0045	.0069
7.699	.0029	.0053	.0134

Coefficients of Correlating Equations

Par	Eqs 1		Eqs 2		Eqs 3	
	coefficient	σ (coeff)	coefficient	σ (coeff)	coefficient	σ (coeff)
1	.1540380507+01	.236-01	.1390110065+01	.780-01	.8461285088+01	.101+00
2	.2959352978+00	.156-01	.7246120694+01	.212+00	-.1057053609+02	.273+00
3	.1089139850+00	.933-02	-.2927728002+01	.239+00	.8438692117+01	.308+00
4	-.3759845723-01	.280-02	.8450975692+00	.134+00	-.3839230943+01	.174+00
5	.4566101958-02	.388-03	-.1452861147+00	.372-01	.9029391473+00	.480-01
6	-.1975054639-03	.198-04	.1147011929-01	.402-02	-.8524940172-01	.519-02

σ (eqs 1) = .291-02
 σ (eqs 2) = .332-02
 σ (eqs 3) = .429-02

Experimental Data Employed in Generation of Correlating Equations

Downes [36]. Isopiestic measurements, reference salt is NaCl. Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.743400	.9622
.815400	.9789
.827900	.9821
.832600	.9835
.885200	.9984
.895400	.9982
1.103200	1.0482
1.166600	1.0654
1.409100	1.1247
1.665700	1.1836
1.856800	1.2252
1.874500	1.2316
1.931100	1.2453
2.081400	1.2779
2.485400	1.3531
2.517000	1.3641
2.784000	1.4124
3.215300	1.4777
3.253000	1.4838

Robinson and Stokes [30]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.114800	.8503
.146300	.8502
.227600	.8613
.293700	.8701
.453700	.8974
.609100	.9287
.982600	1.0203
1.259000	1.0858
1.329000	1.1066
1.539000	1.1583
1.601000	1.1691
1.966000	1.2573
2.306000	1.3286
2.353000	1.3409

Stokes [38]. Isopiestic measurements, reference salt is CaCl_2 . Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
1.838000	1.2283
2.656000	1.3917
2.949000	1.4409
3.163000	1.4750
3.592000	1.5329
4.203000	1.6464
4.305000	1.6138
4.931000	1.6681
5.145000	1.6858
5.550000	1.7160
5.710000	1.7235
5.956000	1.7449
6.705000	1.7870
7.659000	1.8456

Jones et al [10]. Freezing point depression measurements. The ϕ_L and ϕ_C data for MnCl_2 given in table of auxiliary data were used in treating these measurements. Assigned weight is 0.30.

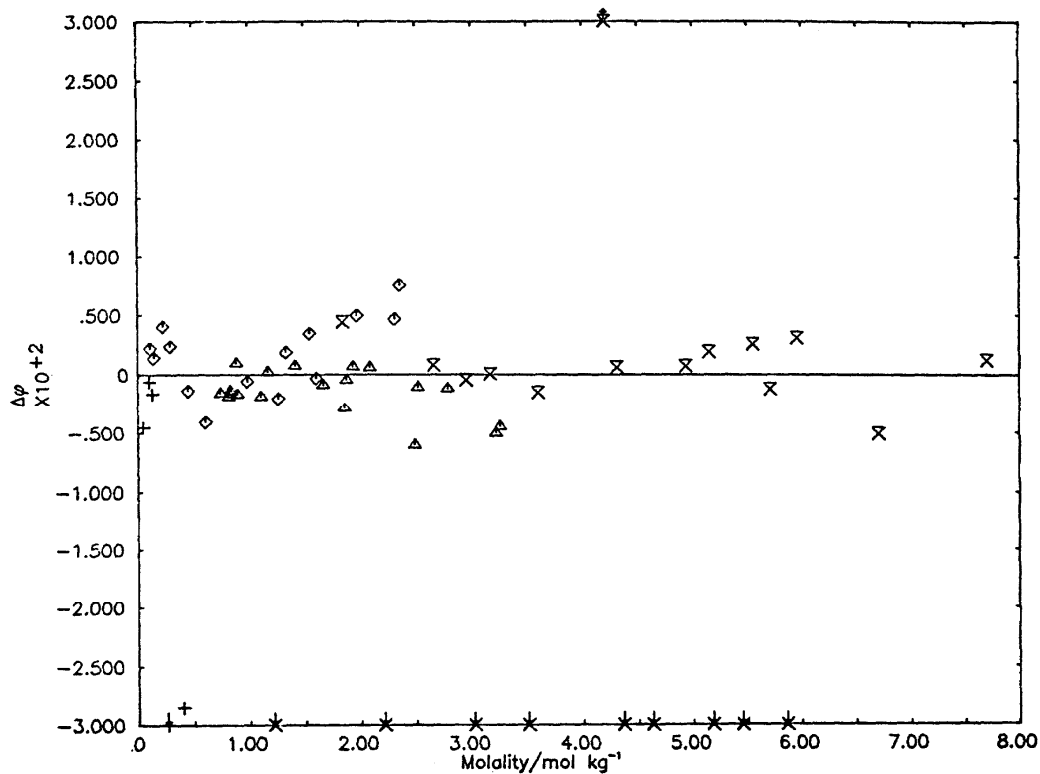
$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.053100	.8536
.106200	.8477
.133400	.8466
.267600	.8173*
.403700	.8599*

Perreu [37]. The vapor pressure measurements at 20°C were adjusted to 25°C using ϕ_L and ϕ_C data for MnCl_2 . Assigned weight is zero.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
1.216000	1.0140
2.209200	1.1100
3.020000	1.2270
3.503000	1.3220
4.363000	1.4320
4.629000	1.4150
5.179000	1.4520
5.451000	1.5030
5.864000	1.5090

Comments

The recent isopiestic data of Downes [36] merge very well with the earlier results of Robinson and Stokes [30]. Perreu's [38] vapor pressure measurements do not appear to be very accurate.



Deviation Plot For MnCl₂: Δφ vs molality

- △ Downes [36], isopiestic vs NaCl
- + Jones et al [10], freezing point depression
- × Perreu [37], vapor pressure
- ◇ Robinson and Stokes [30], isopiestic vs KCl
- * Stokes [38], isopiestic vs CaCl₂

Mn(ClO₄)₂Recommended values for the mean activity and osmotic coefficient of Mn(ClO₄)₂ in H₂O at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8923	.9644	.999948	-1.
.002	.8576	.9531	.999897	-2.
.003	.8340	.9457	.999847	-3.
.004	.8158	.9400	.999797	-4.
.005	.8009	.9356	.999747	-6.
.006	.7884	.9318	.999698	-8.
.007	.7775	.9287	.999649	-9.
.008	.7679	.9260	.999600	-11.
.009	.7593	.9236	.999551	-13.
.010	.7516	.9215	.999502	-15.
.020	.7001	.9094	.999018	-40.
.030	.6709	.9045	.998534	-68.
.040	.6514	.9028	.998050	-99.
.050	.6374	.9028	.997563	-131.
.060	.6269	.9039	.997073	-165.
.070	.6189	.9056	.996580	-201.
.080	.6126	.9079	.996082	-237.
.090	.6076	.9105	.995581	-274.
.100	.6037	.9133	.995076	-311.
.200	.5960	.9498	.989786	-695.
.300	.6141	.9922	.984041	-1071.
.400	.6451	1.0376	.977819	-1416.
.500	.6858	1.0853	.971098	-1720.
.600	.7353	1.1351	.963860	-1975.
.700	.7938	1.1869	.956089	-2175.
.800	.8618	1.2406	.947772	-2317.
.900	.9402	1.2962	.938897	-2395.
1.000	1.0303	1.3535	.929458	-2407.
1.250	1.3169	1.5041	.903377	-2127.
1.500	1.7182	1.6642	.873791	-1371.
1.750	2.2807	1.8325	.840871	-104.
2.000	3.0719	2.0077	.804913	1704.
2.250	4.1885	2.1887	.766320	4077.
2.500	5.7691	2.3741	.725588	7036.
2.750	8.0102	2.5625	.683276	10598.
3.000	11.1896	2.7527	.639984	14777.
3.250	15.6954	2.9432	.596320	19581.
3.456	20.7845	3.0998	.560448	24018.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0003	.0007	.0006
.010	.0019	.0045	.0034
.100	.0048	.0154	.0093
1.000	.0033	.0174	.0179
2.000	.0034	.0170	.0521
3.456	.0061	.0172	.3583

Coefficients of Correlating Equations

Par	Eqs 1		Eqs 2		Eqs 3	
	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$
1	.2274856797+01	.135+00	-.3408616493+01	.491-01	-.1197789929+02	.611+00
2	.6709063717+00	.417-01	.4285009013+01	.577-01	-.1969298517+02	.246+01
3	.2031165429+00	.202-01	-.5286719974+00	.179-01	.2115194354+02	.407+01
4	-.1940042491-01	.325-02			-.1308539555+02	.334+01
5					.4371338080+01	.134+01
6					-.6084240177+00	.209+00

$$\sigma(\text{eqs } 1) = .662-02$$

$$\sigma(\text{eqs } 2) = .659-02$$

$$\sigma(\text{eqs } 3) = .541-02$$

Experimental Data Employed in Generation of Correlating Equations

Libus and Sadowska [31], isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\delta_{298.15}$
.109100	.9090
.364100	1.0302
.644000	1.1546
.790800	1.2351
1.007900	1.3585
1.350500	1.5750

Libus and Sadowska [31], isopiestic measurements, reference salt is $\text{Mg}(\text{ClO}_4)_2$. Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\delta_{298.15}$
2.769400	2.5843
3.101200	2.8336
3.456200	3.0961

Libus and Sadowska [31], isopiestic measurements, reference salt is NaClO_4 . Assigned weight is 1.0.

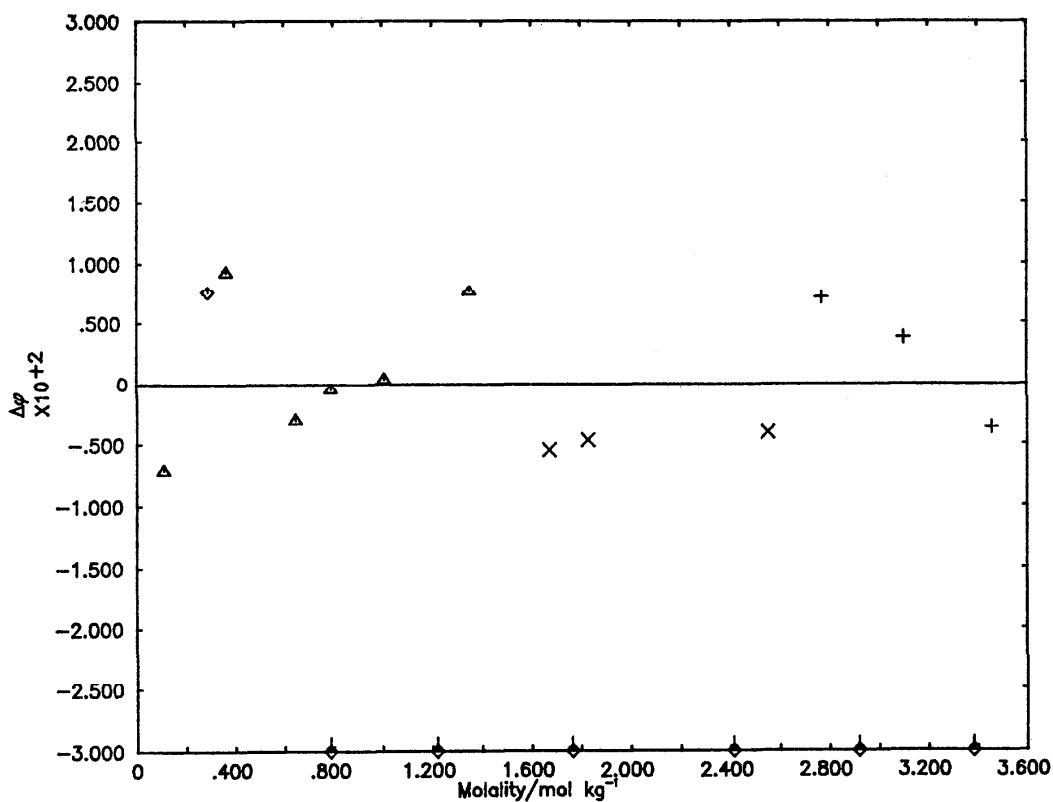
$m/\text{mol}\cdot\text{kg}^{-1}$	$\delta_{298.15}$
1.673400	1.7746
1.829900	1.8831
2.551100	2.4083

Lilich and Andreev [32], vapor pressure measurements. Assigned weight is zero.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\delta_{298.15}$
.289000	.9949
.785000	1.1485
1.218000	1.4378
1.764000	1.7835
2.412000	2.2648
2.919000	2.6250
3.383000	2.9568

Comments

We prefer the isopiestic measurements of Libus and Sadowska [31] over the vapor pressure measurements of Lilich and Andreev [32].



Deviation Plot for $\text{Mn}(\text{ClO}_4)_2$: $\Delta\delta$ vs molality

Δ Libus and Sadowska [31], isopiestic vs KCl

X Libus and Sadowska [31], isopiestic vs NaClO_4

+ Libus and Sadowska [31], isopiestic vs $\text{Mg}(\text{ClO}_4)_2$

◇ Lilich and Andreev [32], vapor pressure

MnBr₂Recommended Values for the mean activity and osmotic coefficient of MnBr₂ in H₂O at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8895	.9628	.999948	-1.
.002	.8526	.9503	.999897	-2.
.003	.8270	.9417	.999847	-3.
.004	.8071	.9351	.999798	-4.
.005	.7906	.9296	.999749	-6.
.006	.7766	.9250	.999700	-8.
.007	.7644	.9210	.999652	-10.
.008	.7536	.9175	.999603	-12.
.009	.7438	.9143	.999555	-14.
.010	.7349	.9115	.999507	-16.
.020	.6743	.8932	.999035	-43.
.030	.6384	.8837	.998568	-74.
.040	.6134	.8780	.998104	-109.
.050	.5946	.8746	.997639	-147.
.060	.5799	.8726	.997174	-186.
.070	.5680	.8715	.996708	-228.
.080	.5581	.8712	.996240	-270.
.090	.5498	.8714	.995770	-314.
.100	.5428	.8720	.995298	-359.
.200	.5080	.8899	.990427	-844.
.300	.5014	.9167	.985247	-1354.
.400	.5068	.9472	.979731	-1865.
.500	.5194	.9800	.973864	-2362.
.600	.5373	1.0146	.967635	-2837.
.700	.5597	1.0504	.961039	-3284.
.800	.5861	1.0874	.954072	-3699.
.900	.6163	1.1252	.946737	-4077.
1.000	.6504	1.1638	.939038	-4418.
1.250	.7524	1.2624	.918251	-5084.
1.500	.8801	1.3625	.895423	-5469.
1.750	1.0363	1.4625	.870818	-5555.
2.000	1.2240	1.5608	.844754	-5334.
2.250	1.4466	1.6562	.817581	-4803.
2.500	1.7070	1.7479	.789653	-3962.
2.750	2.0080	1.8349	.761314	-2817.
3.000	2.3517	1.9167	.732883	-1373.
3.250	2.7397	1.9930	.704642	360.
3.500	3.1728	2.0635	.676829	2371.
3.750	3.6509	2.1283	.649637	4649.
4.000	4.1737	2.1874	.623209	7182.
4.250	4.7403	2.2410	.597645	9958.
4.500	5.3499	2.2897	.573000	12965.
4.750	6.0021	2.3338	.549292	16191.
5.000	6.6970	2.3739	.526504	19625.
5.250	7.4364	2.4107	.504589	23259.
5.500	8.2235	2.4449	.483481	27083.
5.640	8.6871	2.4631	.471980	29305.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0001	.0001	.0001
.010	.0004	.0008	.0006
.100	.0009	.0028	.0015
1.000	.0006	.0028	.0018
2.000	.0006	.0031	.0037
5.000	.0012	.0034	.0228
5.640	.0017	.0033	.0283

Coefficients of Correlating Equations

Par	Eqs 1		Eqs 2		Eqs 3	
	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$
1	.1757388023+01	.233-01	.1300864561+01	.149+00	.9680905506+01	.164+00
2	.4365617797+00	.164-01	.9503350267+01	.602+00	-.1389643524+02	.664+00
3	.1864285858+00	.129-01	-.7575540016+01	.103+01	.1344535212+02	.114+01
4	-.5018215269-01	.502-02	.5369844804+01	.934+00	-.7873653035+01	.103+01
5	.4737509142-02	.913-03	-.2410757811+01	.465+00	.2745269368+01	.513+00
6	-.1481202272-03	.617-04	.5775945205+00	.121+00	-.5349778628+00	.133+00
7			-.5622647504-01	.128-01	.4533196230-01	.141-01

$$\sigma(\text{eqs 1}) = .184-02$$

$$\sigma(\text{eqs 2}) = .174-02$$

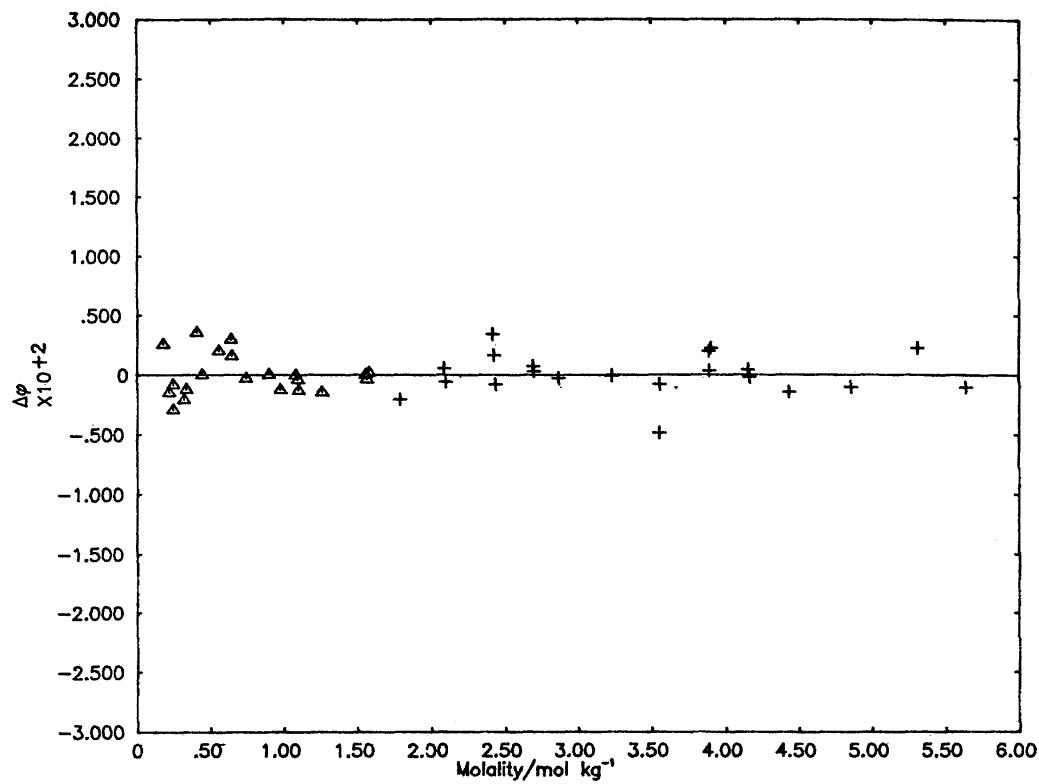
$$\sigma(\text{eqs 3}) = .192-02$$

Experimental Data Employed in Generation of Correlating Equations

Isopiestic data of Libus et al. [32a]. Reference
salt is KCl. Assigned weight is 1.0.

Isopiestic data of Libus et al. [32a]. Reference
salt is $\text{Mg}(\text{ClO}_4)_2$. Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\theta_{298.15}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$\theta_{298.15}$
.177200	.8872	1.787000	1.4751
.216100	.8923	2.090000	1.5961
.243300	.8979	2.100000	1.5988
.245500	.9006	2.416000	1.7210
.317200	.9196	2.427000	1.7232
.334400	.9256	2.436000	1.7240
.405500	.9525	2.695000	1.8169
.445500	.9619	2.701000	1.8185
.558000	1.0019	2.872000	1.8752
.641000	1.0321	3.234000	1.9882
.646000	1.0325	3.554000	2.0731
.746000	1.0670	3.557000	2.0780
.902000	1.1260	3.886000	2.1631
.977000	1.1536	3.893000	2.1631
1.084000	1.1966	3.902000	2.1671
1.100000	1.2025	4.155000	2.2217
1.101000	1.2020	4.166000	2.2234
1.260000	1.2649	4.431000	2.2753
1.558000	1.3858	4.054000	2.3499
1.568000	1.3894	5.311000	2.4215
1.581000	1.3952	5.640000	2.4621



Deviation Plot for MnBr_2 : $\Delta\phi$ vs molality

▲ Libus et al. [32a], isopiestic vs KCl

+ Libus et al. [32a], isopiestic vs $\text{Mg}(\text{ClO}_4)_2$

UO₂Cl₂

Recommended Values for the mean activity and osmotic coefficient of UO₂Cl₂ in H₂O at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8885	.9623	.999948	-1.
.002	.8508	.9494	.999897	-2.
.003	.8245	.9404	.999848	-3.
.004	.8040	.9333	.999798	-5.
.005	.7871	.9276	.999749	-6.
.006	.7726	.9226	.999701	-8.
.007	.7600	.9184	.999653	-10.
.008	.7487	.9146	.999605	-12.
.009	.7386	.9112	.999557	-14.
.010	.7293	.9082	.999509	-17.
.020	.6662	.8882	.999040	-44.
.030	.6285	.8776	.998578	-76.
.040	.6024	.8712	.998118	-112.
.050	.5827	.8673	.997659	-151.
.060	.5674	.8650	.997199	-193.
.070	.5549	.8637	.996738	-236.
.080	.5447	.8633	.996274	-280.
.090	.5360	.8634	.995809	-326.
.100	.5287	.8641	.995341	-373.
.200	.4929	.8832	.990498	-878.
.300	.4859	.9111	.985336	-1412.
.400	.4903	.9415	.975853	-1946.
.500	.5009	.9726	.974060	-2469.
.600	.5156	1.0039	.967971	-2973.
.700	.5335	1.0350	.961599	-3453.
.800	.5540	1.0659	.954958	-3906.
.900	.5766	1.0965	.948062	-4331.
1.000	.6013	1.1267	.940924	-4725.
1.250	.6712	1.2004	.922107	-5569.
1.500	.7522	1.2715	.902056	-6205.
1.750	.8443	1.3400	.880964	-6627.
2.000	.9479	1.4060	.859010	-6834.
2.250	1.0634	1.4694	.836367	-6827.
2.500	1.1913	1.5304	.813200	-6606.
2.750	1.3322	1.5889	.789661	-6177.
3.000	1.4868	1.6450	.765893	-5541.
3.174	1.6026	1.6826	.749286	-4979.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0000	.0001	.0001
.010	.0003	.0006	.0005
.100	.0010	.0028	.0015
1.000	.0008	.0044	.0026
2.000	.0009	.0040	.0038
3.174	.0020	.0049	.0079

Coefficients of Correlating Equations

Par	Eqs 1		Eqs 2		Eqs 3	
	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$
1	.1533848886+01	.160-01	.1072602605+01	.251+00	.1003513394+02	.256+00
2	.6323765000+00	.621-02	.9900796364+01	.104+01	-.1546776012+02	.106+01
3	-.2673338794-01	.139-02	-.7382026414+01	.176+01	.1603785393+02	.179+01
4			.4277602702+01	.149+01	-.9836311886+01	.152+01
5			-.1428675849+01	.616+00	.3226020411+01	.629+00
6			.2009327490+00	.100+00	-.4360865496+00	.102+00

$$\sigma(\text{eqs 1}) = .287-02$$

$$\sigma(\text{eqs 2}) = .281-02$$

$$\sigma(\text{eqs 3}) = .287-02$$

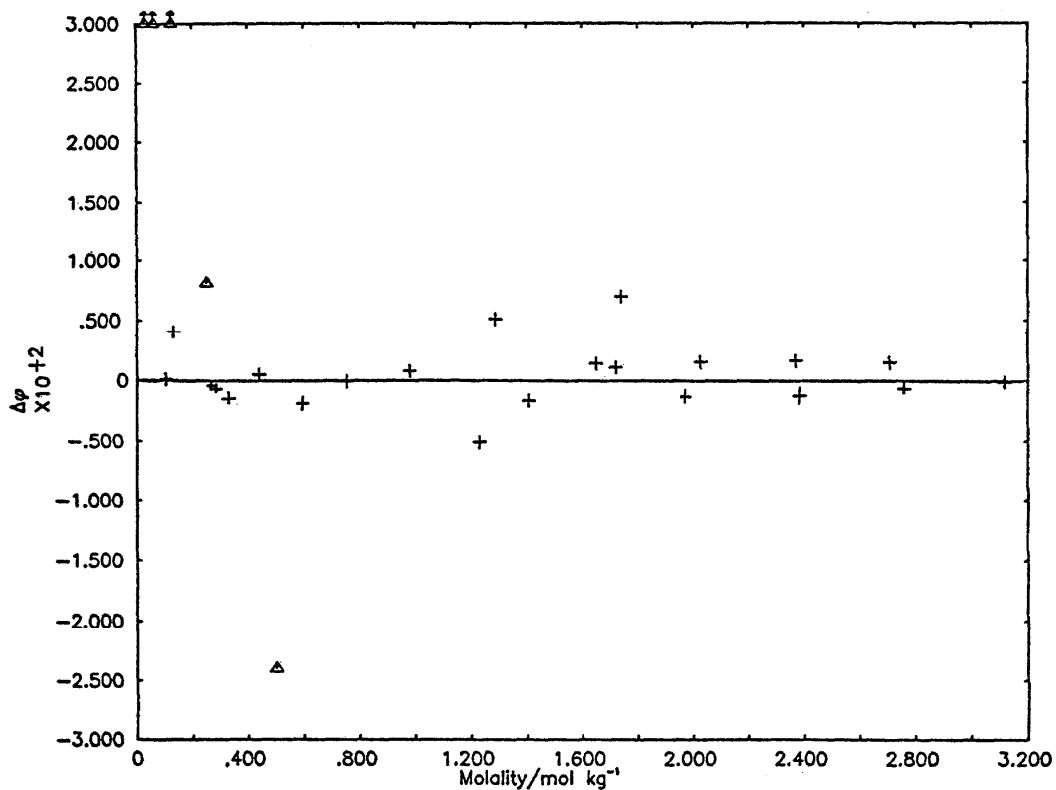
Experimental Data Employed in Generation of Correlating Equations

Dittrich [39]. Freezing point depression measurements. The ϕ_L and ϕ_C data for $ZnCl_2$ given in the table of auxiliary data were used to treat these measurements. Assigned weight is zero.

$m/mol \cdot kg^{-1}$	$\phi_{298.15}$
.031290	.9629
.062640	.9304
.125500	.9032
.252200	.9067
.509200	.9528

Robinson and Lim [40]. Isopiestic measurements, reference salt is $CaCl_2$. Assigned weight is 1.0.

$m/mol \cdot kg^{-1}$	$\phi_{298.15}$
.104700	.8659
.132800	.8738
.269000	.9028
.359800	.9281
.386400	.9350
.456900	.9713
.651200	1.0172
.808700	1.0678
1.037000	1.1378
1.288000	1.2056
1.344000	1.2319
1.465000	1.2594
1.706000	1.3289
1.777000	1.3477
1.757000	1.3590
2.030000	1.4118
2.084000	1.4285
2.427000	1.5139
2.442000	1.5147
2.765000	1.5933
2.818000	1.6032
3.174000	1.6820



Deviation Plot For UO_2Cl_2 : $\Delta\phi$ vs molality

- ▲ Dittrich [39], freezing point depression
- + Robinson and Lim [40], isopiestic vs $CaCl_2$

$$\text{UO}_2(\text{ClO}_4)_2$$

Recommended Values for the mean activity and osmotic coefficient of $\text{UO}_2(\text{ClO}_4)_2$ in H_2O at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8911	.9637	.999948	-1.
.002	.8555	.9520	.999897	-2.
.003	.8311	.9441	.999847	-3.
.004	.8123	.9381	.999797	-4.
.005	.7969	.9333	.999748	-6.
.006	.7838	.9293	.999699	-8.
.007	.7725	.9259	.999650	-10.
.008	.7625	.9230	.999601	-12.
.009	.7535	.9204	.999552	-14.
.010	.7455	.9181	.999504	-16.
.020	.6917	.9048	.999022	-41.
.030	.6613	.8957	.998542	-70.
.040	.6413	.8980	.998060	-102.
.050	.6271	.8984	.997575	-136.
.060	.6167	.9000	.997086	-171.
.070	.6088	.9025	.996591	-208.
.080	.6030	.9056	.996092	-245.
.090	.5985	.9092	.995587	-283.
.100	.5953	.9131	.995077	-321.
.200	.5974	.9624	.989651	-710.
.300	.6300	1.0202	.983595	-1076.
.400	.6799	1.0821	.976777	-1392.
.500	.7443	1.1473	.969472	-1646.
.600	.8232	1.2153	.961357	-1829.
.700	.9180	1.2858	.952518	-1933.
.800	1.0307	1.3588	.942943	-1954.
.900	1.1642	1.4340	.932626	-1887.
1.000	1.3219	1.5113	.921566	-1727.
1.250	1.8526	1.7132	.890706	-898.
1.500	2.6587	1.9258	.855453	580.
1.750	3.8902	2.1472	.816210	2749.
2.000	5.7818	2.3754	.773549	5641.
2.250	8.6998	2.6086	.728175	9282.
2.500	13.2113	2.8447	.680886	13691.
2.750	20.1874	3.0817	.632529	18883.
3.000	30.9495	3.3178	.583952	24867.
3.250	47.4706	3.5508	.535962	31646.
3.500	72.6396	3.7788	.489292	39219.
3.750	110.5832	3.9997	.444575	47579.
4.000	167.0204	4.2116	.402325	56712.
4.250	249.5856	4.4125	.362930	66603.
4.500	367.9998	4.6004	.326656	77229.
4.750	533.9081	4.7732	.293651	88562.
5.000	760.1365	4.9289	.263967	100570.
5.250	1059.1089	5.0655	.237571	113215.
5.458	1370.2327	5.1631	.218048	124190.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0003	.0007	.0006
.010	.0015	.0044	.0033
.100	.0055	.0165	.0098
1.000	.0035	.0221	.0293
2.000	.0040	.0198	.1147
5.000	.0077	.0221	16.8065
5.458	.0132	.0227	31.1295

Coefficients of Correlating Equations

Par	Eqs 1		Eqs 2		Eqs 3	
	coefficient	σ (coeff)	coefficient	σ (coeff)	coefficient	σ (coeff)
1	.2012602139+01	.103+00	.3205380858+01	.375-01	.9803235409+01	.243+00
2	.9632962957+00	.299-01	.4906119968+01	.367-01	-.1086055278+02	.581+00
3	.2593022966+00	.102-01	-.7059660088+00	.944-02	.7492399404+01	.541+00
4	-.2898939350-01	.113-02			-.2426592647+01	.223+00
5					.2914402734+00	.339-01

σ (eqs 1) = .190-01
 σ (eqs 2) = .197-01
 σ (eqs 3) = .191-01

Experimental Data Employed in Generation of Correlating Equations

Boyd [41]. Isopiestic measurements. Reference salt is NaCl. Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.037213	.9251 *
.069587	.9193
.111230	.9227
.210950	.9704
.299500	1.0231
.624250	1.2311

Rush and Johnson [42]. Isopiestic measurements. Reference electrolyte is H_2SO_4 . Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
4.448700	4.6039
3.940000	4.1937
3.371000	3.6882
3.310300	3.6292
2.746300	3.1077
2.503300	2.8751
2.185300	2.5728
1.857000	2.2568
1.663100	2.0775
1.327700	1.7726
1.262000	1.7184
.943400	1.4622
.671870	1.2748
3.538000	3.8325
3.496000	3.7966
3.027000	3.3630
2.966700	3.3089
2.524000	2.8889
2.283700	2.6608
2.051000	2.4383
1.715700	2.1214
1.600900	2.0154
1.264300	1.7157
1.236600	1.6945
.917700	1.4415
.673400	1.2747

Robinson and Lim [40]. Isopiestic measurements. Reference salt is CaCl_2 . Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.106100	.9152
.154900	.9447
.207800	.9669
.287000	1.0169
.363400	1.0605
.380600	1.0719
.573300	1.1965
.762700	1.3299
.965700	1.4777
1.329000	1.7623
1.602000	1.9912
1.859000	2.2174
1.992000	2.3435
2.591000	2.8994
2.749000	3.0551
2.869000	3.1732
3.289000	3.5580
3.687000	3.8950
3.907000	4.0849
4.242000	4.3677
4.601000	4.6467
4.853000	4.8270
5.039000	4.9452
5.179000	5.0267
5.458000	5.1883

Rush and Johnson [42]. Isopiestic measurements. Reference electrolyte is NaCl. Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
1.886000	2.2741
1.670700	2.0757
1.299600	1.7531
.966900	1.4863
.701600	1.2895
.494300	1.1474
.352800	1.0639

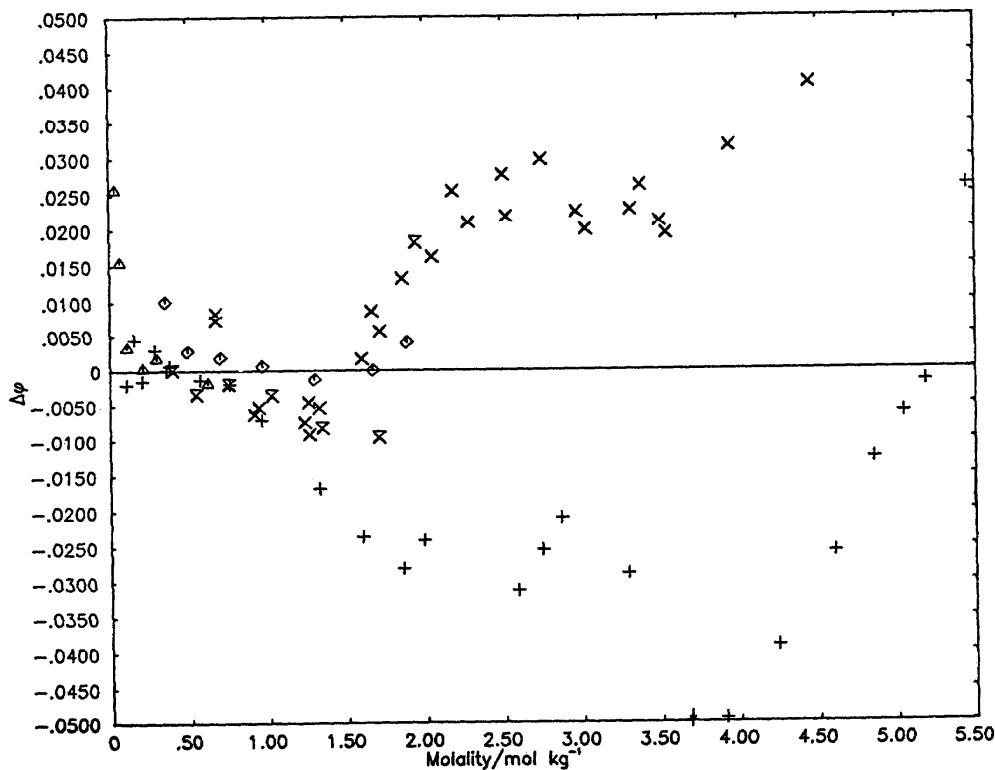
Rush and Johnson [42]. Isopiestic measurements. Reference electrolyte is $\text{Na}(\text{ClO}_4)_2$. Assigned weight is 1.0.

Schwabe et al. [42]. Solvent extraction technique. Assigned weight is zero.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$	$m/\text{mol}\cdot\text{kg}^{-1}$	$\gamma/\gamma_{\text{ref}}$
1.946000	2.3433	0.1	0.30
1.707700	2.0991	0.5	0.24
1.347000	1.7860	1.0	0.31
1.027600	1.5295	2.0	0.77
.756800	1.3255	3.0	2.42
.549000	1.1778	4.0	7.75
.394400	1.0799	5.0	23.32
		5.44	35.94

Comments

The various isopiestic investigations are in reasonable agreement up to a molality of about $1.2 \text{ mol}\cdot\text{kg}^{-1}$. The more serious and systematic deviations between the results of Robinson and Lim [40] and Rush and Johnson [42] at the higher molalities were attributed by the latter workers to experimental uncertainties of about 0.3 percent in the molalities of the solutions. They [42] also state that this uncertainty is comparable to their experimental imprecision. Schwabe et al. [43] report a set of activity coefficients that differs significantly from those obtained from the data of the other investigators. Unfortunately, Schwabe et al. [43] do not give their essential experimental data. We have given their results zero weight.



Deviation Plot For $\text{UO}_2(\text{ClO}_4)_2$: $\Delta\phi$ vs molality

- ▲ Boyd [41], isopiestic vs NaCl
- + Robinson and Lim [40], isopiestic vs CaCl_2
- × Rush and Johnson [42], isopiestic vs H_2SO_4
- ◇ Rush and Johnson [42], isopiestic vs NaCl
- ✕ Rush and Johnson [42], isopiestic vs $\text{Na}(\text{ClO}_4)_2$

$\text{UO}_2(\text{NO}_3)_2$ Recommended Values for the mean activity and osmotic coefficient of $\text{UO}_2(\text{NO}_3)_2$ in H_2O at 298.15 K

$m/\text{mol}\cdot\text{kg}^{-1}$	γ	ϕ	a_w	$\Delta G^{\text{ex}}/\text{J}\cdot\text{kg}^{-1}$
.001	.8876	.9618	.999948	-1.
.002	.8492	.9485	.999897	-2.
.003	.8226	.9393	.999848	-3.
.004	.8017	.9321	.999799	-5.
.005	.7845	.9262	.999750	-6.
.006	.7698	.9212	.999701	-8.
.007	.7565	.9169	.999653	-10.
.008	.7455	.9130	.999605	-12.
.009	.7353	.9096	.999558	-15.
.010	.7260	.9066	.999510	-17.
.020	.6629	.8873	.999041	-44.
.030	.6262	.8779	.998578	-77.
.040	.6012	.8731	.998114	-114.
.050	.5829	.8708	.997650	-153.
.060	.5689	.8700	.997183	-194.
.070	.5577	.8703	.996713	-236.
.080	.5488	.8714	.996240	-280.
.090	.5414	.8729	.995763	-326.
.100	.5353	.8749	.995283	-372.
.200	.5088	.9028	.990289	-860.
.300	.5079	.9348	.984962	-1365.
.400	.5171	.9669	.979313	-1863.
.500	.5325	1.0001	.973336	-2343.
.600	.5527	1.0342	.967018	-2799.
.700	.5771	1.0695	.960347	-3224.
.800	.6054	1.1057	.953316	-3615.
.900	.6375	1.1428	.945928	-3969.
1.000	.6733	1.1806	.938188	-4284.
1.250	.7791	1.2759	.917413	-4885.
1.500	.9072	1.3695	.894915	-5208.
1.750	1.0561	1.4578	.871201	-5248.
2.000	1.2231	1.5381	.846830	-5008.
2.250	1.4039	1.6084	.822347	-4504.
2.500	1.5935	1.6678	.798237	-3754.
2.750	1.7860	1.7159	.774897	-2780.
3.000	1.9754	1.7528	.752624	-1606.
3.250	2.1565	1.7791	.731614	-256.
3.500	2.3250	1.7959	.711968	1244.
3.750	2.4781	1.8045	.693701	2874.
4.000	2.6146	1.8061	.676758	4612.
4.250	2.7348	1.8022	.661023	6442.
4.500	2.8405	1.7945	.646336	8349.
4.750	2.9344	1.7843	.632502	10321.
5.000	3.0199	1.7731	.619310	12349.
5.250	3.1009	1.7621	.606538	14429.
5.500	3.1811	1.7524	.593972	16557.
5.511	3.1847	1.7521	.593421	16652.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\sigma(\phi)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0001	.0002	.0002
.010	.0006	.0014	.0010
.100	.0024	.0065	.0035
1.000	.0017	.0073	.0049
2.000	.0015	.0078	.0096
5.000	.0029	.0086	.0259
5.511	.0054	.0088	.0280

Coefficients of Correlating Equations

Par	Eqs 1		Eqs 2		Eqs 3	
	coefficient	σ (coeff)	coefficient	σ (coeff)	coefficient	σ (coeff)
1	.1504157716+01	.190-01	.4014072256+00	.118+00	.9175618892+01	.953-01
2	.6432902305+00	.235-01	.1197224094+02	.502+00	-.1152406753+02	.405+00
3	.1099184609+00	.158-01	-.9637745838+01	.784+00	.9341722774+01	.632+00
4	-.4895740998-01	.431-02	.5503177528+01	.572+00	-.4176826645+01	.461+00
5	.4103437792-02	.392-03	-.1736483942+01	.198+00	.9071521089+00	.160+00
6			.2224512292+00	.263-01	-.7261880370-01	.212-01

σ (eqs 1) = .113-01
 σ (eqs 2) = .126-01
 σ (eqs 3) = .102-01

Experimental Data Employed in Generation of Correlating Equations

Apelblat [44a]. Freezing point depression measurements (the author reports freezing point data up to a molality of $2.07 \text{ mol} \cdot \text{kg}^{-1}$). The ϕ_1 data for $\text{Zn}(\text{NO}_3)_2$ and the ϕ_c data for $\text{UO}_2(\text{NO}_3)_2$ given in the table of auxiliary data were used in treating these data. The results seem highly erratic and do not merge well with either the isopiestic or the solvent extraction data. We prefer the latter measurements and have assigned this data set a weight of zero.

$m/\text{mol} \cdot \text{kg}^{-1}$	$\phi_{298.15}$
0.00400	1.6690
0.00500	1.5389
0.00880	1.1196
0.00990	1.1542
0.01000	1.1606
0.01250	1.2348
0.01760	1.0974
0.01850	0.9665
0.02000	0.9835
0.02310	0.9058
0.02410	1.1433
0.02610	1.0145
0.02790	0.8977
0.03000	1.0381
0.03000	0.9239
0.03990	0.9833
0.05920	0.9282
0.08000	0.9407
0.09720	0.9188
0.16300	1.1065

Dittrich [39]. Freezing point depression measurements. The ϕ_1 data for $\text{Zn}(\text{NO}_3)_2$ and the ϕ_c data for $\text{UO}_2(\text{NO}_3)_2$ given in the table of auxiliary data were used in treating these data. Assigned weight is zero.

$m/\text{mol} \cdot \text{kg}^{-1}$	$\phi_{298.15}$
.031310	.9508
.062720	.9235
.125900	.8931
.253600	.9019
.515100	.9545

Robinson and Lim [40]. Isopiestic measurements, reference salt is CaCl_2 . Assigned weight is 1.0

$m/\text{mol} \cdot \text{kg}^{-1}$	$\phi_{298.15}$
.973600	1.1747
1.092000	1.2162
1.216000	1.2688
1.371000	1.3109
1.595000	1.3905
1.724000	1.4396
2.008000	1.5334
2.043000	1.5480
2.282000	1.6144
2.356000	1.6316
2.473000	1.6616
2.574000	1.6821
2.641000	1.6899
2.664000	1.6939
2.793000	1.7283
2.942000	1.7486
2.946000	1.7362
3.035000	1.7620
3.153000	1.7767
3.401000	1.7811
3.587000	1.7086 *
2.245000	1.6082
2.422000	1.6568
2.661000	1.7051
3.127000	1.7658
3.191000	1.7750
3.242000	1.7809
3.523000	1.8010
3.894000	1.8082
4.306000	1.8035
4.481000	1.7923
4.810000	1.7809
4.971000	1.7773
5.106000	1.7654
5.319000	1.7546
5.511000	1.7565
.101000	.8699
.169100	.8864
.303400	.9276
.487900	.9879
.548400	1.0094
.773700	1.0899
1.041000	1.1961
1.288000	1.2792
1.522000	1.3670
1.823000	1.4733
2.297000	1.6168

Robinson, Wilson, and Ayling [33]. Reference salt is KCl. Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
0.093000	0.8871
0.115600	0.8884
0.249200	0.9260
0.286500	0.9314
0.298200	0.9318
0.470700	0.9891
0.551000	0.9090 *
0.663200	1.0606
0.755700	1.0962
0.865000	1.1346
1.020000	1.1917
1.116000	1.2336
1.219000	1.2756
1.252000	1.2809
1.453000	1.3533
1.457000	1.3618
1.493000	1.3672
1.505000	1.3714
1.545000	1.3893
1.654000	1.4318
1.697000	1.4499
1.759000	1.4677
1.887000	1.5119
2.035000	1.5575

Mikhailov and Torgov [44]. Solvent extraction technique where uranyl nitrate is allowed to equilibrate between an aqueous phase and an organic solvent (0.1 molar tri-n-butyl phosphate in benzene). Assigned weight is 0.70.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\gamma/\gamma_{\text{ref}}$
0.012340	1.0000
0.017110	0.9294
0.025770	0.8619
0.034370	0.8423
0.042980	0.8080
0.051580	0.7888
0.068700	0.7663
0.085900	0.7498
0.116700	0.7201
0.136000	0.7054
0.155200	0.6958
0.174200	0.6885
0.193200	0.6799

Mikhailov and Torgov [44]. Solvent extraction technique where uranyl nitrate is allowed to equilibrate between an aqueous phase and an organic solvent (0.1 molar tri-n-butyl phosphate in CCl_4). Assigned weight is 0.70.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\gamma/\gamma_{\text{ref}}$
0.012840	1.0000
0.017130	0.9528
0.025780	0.8900
0.034420	0.8670
0.043070	0.8507
0.051720	0.8142
0.060380	0.8083
0.069050	0.7900
0.077700	0.7863
0.086220	0.7773
0.104700	0.7496
0.115700	0.7479
0.125600	0.7342
0.135900	0.7307
0.146500	0.7156
0.156200	0.7085
0.167400	0.7194
0.176400	0.7126
0.192700	0.7029

Comments

The method used by Mikhailov and Torgov [44] requires some discussion. They allowed uranyl nitrate to equilibrate between water and an organic solvent, either benzene or carbon tetrachloride, containing an additional solute (tri-n-butyl phosphate (TBP)) that serves as an "extracting agent" to increase the concentration of the $\text{UO}_2(\text{NO}_3)_2$ in the organic phase. The equilibrium may be represented as: $\text{UO}_2^{2+}(\text{aq}) + 2\text{NO}_3^-(\text{aq}) + 2\text{TBP}(\text{org}) = \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}(\text{org})$ where (aq) and (org) denote aqueous and organic phases, respectively. For the above equilibrium we write

$$K = \frac{m_u \gamma_u}{4m_{\pm}^3 \gamma_{\pm}^3 \gamma_{\text{TBP}}^2 (m_{\text{TBP}} - 2m_u)^2}$$

Comments (continued)

Assuming that $K\gamma_{\text{TBP}}^2/\gamma_{\text{U}} = K'$ a constant, we have $m_{\text{U}} = 4K' (m\gamma_{\pm})^3 (m_{\text{TBP}} - 2m_{\text{U}})^2$ where m_{U} and m are the molalities of $\text{UO}_2(\text{NO}_3)_2$ in the organic phase and aqueous phases, respectively; m_{TBP} is the molality of TBP in the organic phase; γ_{U} and γ_{\pm} are the activity coefficients of $\text{UO}_2(\text{NO}_3)_2$ in the organic and aqueous phases, respectively; and γ_{TBP} is the activity coefficient of tri-n-butyl phosphate in the aqueous phase. It is then possible to calculate values of $\gamma/\gamma_{\text{ref}}$:

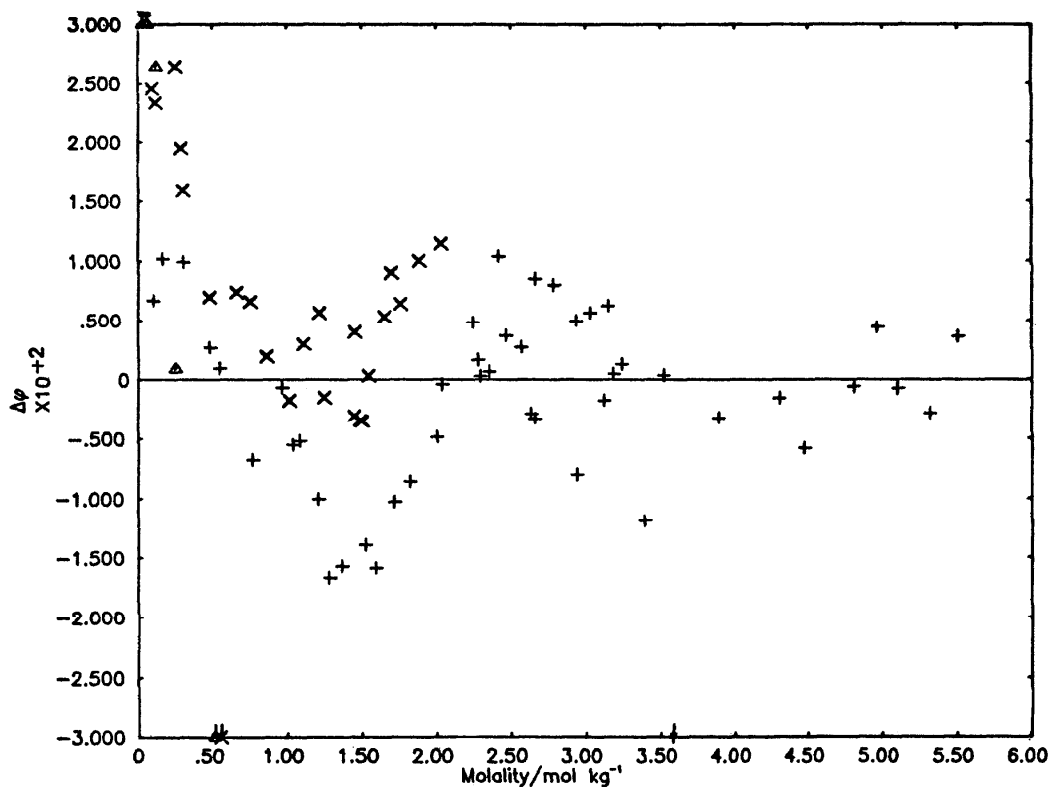
$$\gamma_{\pm} = \left[\frac{m_{\text{U}}}{4K'm^3(m_{\text{TBP}} - m_{\text{U}})^2} \right]^{1/3} = \beta^{1/3} \left(\frac{1}{K'} \right)^{1/3}$$

$$\gamma/\gamma_{\text{ref}} = (\beta/\beta_{\text{ref}})^{1/3}$$

$$\text{where } \beta \equiv \frac{m_{\text{U}}}{4m^3(m_{\text{TBP}} - 2m_{\text{U}})^2}$$

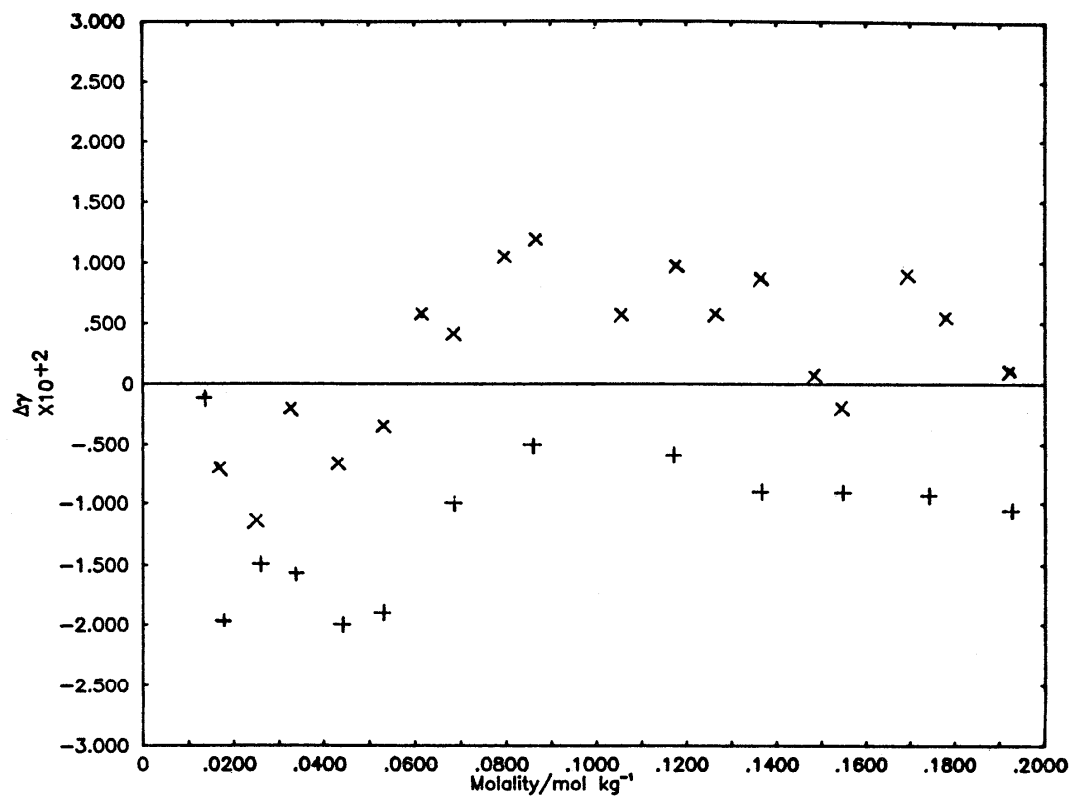
We find that the results of Mikhailov and Torgov [44] are in reasonable agreement with the results of Robinson et al. [33,40].

The results of Glueckauf, McKay and Mathieson [45] who also used a solvent extraction procedure, pertain to a mixed electrolyte system, and hence were not considered in this evaluation.



Deviation Plot for $\text{UO}_2(\text{NO}_3)_2$: $\Delta\phi$ vs molality

- ▲ Dittrich [39], freezing point depression
- + Robinson and Lim [40], isopiestic vs CaCl_2
- × Robinson, Wilson and Ayling [33], isopiestic vs KCl .



Deviation Plot For $\text{UO}_2(\text{NO}_3)_2$; $\Delta\gamma$ vs molality

- + Mikhailov and Torgov [44], solvent extraction using benzene
- × Mikhailov and Torgov [44], solvent extraction using carbon tetrachloride

2.3. Systems Not Treated

Neither the freezing point depression data of Jones et al. [10] nor the vapor pressure measurements of Ewing, Glick, and Rasmussen [11] seem reliable enough to us to generate a set of recommended values for γ and ϕ for $\text{Mn}(\text{NO}_3)_2$. Hence, we have not treated this system. A similar situation exists for uranyl acetate where we have only the few old freezing point depression measurements of Dittrich [12]. Johnson et al. [13] and Johnson and Kraus [14] report, respectively, ultracentrifuge measurements and freezing point depression measurements for uranyl fluoride. Unfortunately, in the ultracentrifuge work the authors, contrary to their own statement, do not give the essential experimental data, but only give values of $\gamma/\gamma_{\text{ref}}$ obtained on the assumption that UO_2F_2 is a non-electrolyte, i.e., $\nu = 1$. Johnson and Kraus [14] also kept ν equal to 1 when treating their freezing point depression data, citing conductance data [14] and their own freezing point depression measurements as evidence for this assumption.

2.4. Previous Compilations and Evaluations

Previous evaluations and compilations of the activity and osmotic coefficients for many of the systems dealt with herein may be found in the books by Harned and Owen [46] and Robinson and Stokes [47], and in the papers of Wu and Hamer [48] and Pitzer and Mayorga [49]. None of these previous reviews has presented data for PbCl_2 , $\text{Cu}(\text{ClO}_4)_2$, $\text{Cu}(\text{C}_7\text{H}_7\text{O}_5\text{S})_2$, or $\text{Mn}(\text{ClO}_4)_2$.

As discussed previously [3,5], the tables of Robinson and Stokes [47] appear to be exclusively based upon their own isopiestic measurements; Harned and Owen [46] also based their tables upon earlier calculations performed by Robinson and Stokes [50] which were also based upon these same isopiestic measurements. For these compounds, the coefficients of the equations of Pitzer and Mayorga [49] are based exclusively upon the smoothed osmotic

coefficients given by Robinson and Stokes [47]. Wu and Hamer [48] utilized a larger data base than the other compilations [46,47,49], but, unfortunately, did not state how the various data sources were weighted to obtain their final tables of recommended values. The average difference between our recommended values of the activity coefficient at the maximum molality for which comparisons may be made with the other compilations is 2.4 percent; the maximum difference occurs for $\text{Pb}(\text{ClO}_4)_2$, there is an 8.8 percent difference between our recommended value for γ at $12.0 \text{ mol} \cdot \text{kg}^{-1}$ and that given by Wu and Hamer [48]. We are unable to explain this discrepancy.

3. Auxiliary Data

Osmotic Coefficient Data

Evaluated data for several reference systems were needed in treating the isopiestic data. These systems and the sources of the evaluated data are: KCl [1], NaCl [1], H_2SO_4 [4], CaCl_2 [2], and NaClO_4 [1].

For $\text{Mg}(\text{ClO}_4)_2$ we have used equation (1b) with the coefficients $B = 2.03029792$, $C = 0.634422465$, $D = 0.20312563$, $E = 0.019262859$, and $F = -0.0000902002$. These coefficients were obtained by a weighted fit [50a] of the isopiestic data of Stokes and Levien [50b] and the freezing point depression data of Nicholson and Felsing [50c].

Relative Apparent Molal Enthalpy Data

The coefficients for the equation $\Phi_r/J \cdot \text{mol}^{-1} = \sum_{i=1}^n \alpha_i m^{i/2}$ were obtained by least-squares fits to the values of Φ_L calculated from the enthalpies of formation as a function of the molality as given in NBS Technical Note 270-4 [51] for ZnCl_2 , $\text{Zn}(\text{NO}_3)_2$, MnCl_2 , and $\text{Mn}(\text{NO}_3)_2$. The coefficients for $\text{Cu}(\text{ClO}_4)_2$ were obtained by a fit to the data of Gier and Vanderzee [52]. The coefficients are given in table 1.

TABLE 1. Coefficients used to calculate relative apparent molal enthalpies

System	Range of validity molality/mol \cdot kg $^{-1}$	α_1	α_2	α_3	α_4	α_5	α_6	α_7	α_8
ZnCl_2	0 to 1.39	10263.4	3105.56	4776.8	-2953.43				
$\text{Zn}(\text{NO}_3)_2$	0 to 6.94	10263.4	-11248.1	-47636.7	129340.0	-129489.0	64295.4	-15827.2	1543.31
$\text{Cu}(\text{ClO}_4)_2$	0 to 3.70	10263.4	-29187.2	36621.8	30493.3	-89144.2			
MnCl_2	0 to 1.39	10263.4	13829.8	-161829.0	446130.0	-478966.0	175850.0		
$\text{Mn}(\text{NO}_3)_2$	0.28 to 22.2	-2072.64	4024.91	-470.219	14.4741				

Apparent Molal Heat Capacity Data

The coefficients for the equation $\Phi_C/J \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = \Phi_C^\circ + \sum_{i=1}^N \beta_i m^{i/2}$ are given in table 2.

TABLE 2. Coefficients used to calculate apparent molal heat capacities.

System	Range of validity molality/mol·kg ⁻¹	Φ_C°	β_1	β_2	Reference
Cu(ClO ₄) ₂	0.05 to 0.20	-72.4	150.38	-93.7	[53]
Zn Cl ₂	0.25 to 17.12	-169.4	147.63	-11.69	[54]
MnCl ₂	0.05 to 3.85	-232.3	150.38	-41.43	[55]
UO ₂ (NO ₃) ₂	0.04 to 0.89	-129.4	230.16		[55a]

Additional auxiliary data follow:

$$\Delta H_{\text{fus}}^\circ = 6008 \text{ J} \cdot \text{mol}^{-1} [56]$$

$$\Delta C_{\text{fus}}^\circ = 38.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} [56]$$

$$\Delta b = -0.197 \text{ J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1} [56]$$

$$T_{\text{fus}} = 273.15 \text{ K for water [8]}$$

$$R = 8.31441 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} [57]$$

$$F = 96484.56 \text{ C} \cdot \text{mol}^{-1} [57]$$

$$A = 1.17625 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} [2]$$

$$P^\circ = 3168.6 \text{ Pa (23.7627 torr) for water at 25 }^\circ\text{C [58]}$$

$$B_T = -992 \text{ cm}^3 \cdot \text{mol}^{-1} \text{ at } 25^\circ\text{C [59]}$$

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6. Glossary of Symbols

a_w	activity of water	ΔG^{ex}	the excess Gibbs energy of a solution containing one kilogram of solvent
Δb	$(\partial \Delta \bar{C}_p / \partial T)_p$	ΔH°_{fus}	the enthalpy of fusion of the pure solvent at the freezing temperature of the pure solvent
c_B or c	concentration of solute substance B	I_m or I	ionic strength: $(I_m = \frac{1}{2} \sum_i m_i z_i^2)$
m_B or m	molality of solute substance B	P	vapor pressure of a solution
z_B	charge number of an ion B	P°	vapor pressure of pure solvent
A	constant in Debye-Hückel limiting law	R	molar gas constant
A_1	$ z_+ z_- A$	T	thermodynamic or absolute temperature
A_2	$\frac{(\sum_i \nu_i z_i^3)^2}{3\nu \sum_i (\nu_i z_i^2)} A^2$	T_{fus}	absolute temperature of fusion of pure solvent
A_i	coefficients in a specified equation	α_i	coefficients in a specified equation
B, C, D, E, \dots	coefficients in eqs (1)	β_i	coefficients in a specified equation
B_i	coefficients in a specified equation	γ_{\pm} or γ	activity coefficient, molality basis
B_T	the second virial coefficient for water vapor	ν_i	number of ions of species i formed from one molecule of solute assuming complete dissociation
ΔC°_{fus}	the heat capacity change accompanying the fusion of the pure solvent at the freezing temperature of the pure solvent	ν	total number of ions formed from one molecule of solute assuming complete dissociation: $[\nu = \sum_i \nu_i]$
$\Delta \bar{C}_p$	the different between the partial molal heat capacity of the solvent in a solution and the molal heat capacity of the solid solvent at the freezing temperature of the solution	σ	standard deviation
F	the Faraday constant	ϕ or φ	osmotic coefficient
		Φ_G	apparent molal heat capacity
		Φ_L	relative apparent molal enthalpy