

Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Iron Chloride and the Bi-Univalent Compounds of Nickel and Cobalt

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A critical evaluation of the mean activity and osmotic coefficients in aqueous solutions of iron chloride, nickel chloride, perchlorate, and nitrate and twenty-nine bi-univalent compounds of cobalt at 298.15 K is presented. Osmotic coefficients were calculated from direct vapor pressure measurements, from isopiestic measurements, from freezing point depression measurements, and from vapor pressure osmometry measurements. 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.

Key words: Activity coefficient; cobalt; critical evaluation; electrolyte; excess Gibbs energy; iron; nickel; osmotic coefficients; solutions; thermodynamic properties.

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1. Introduction

This paper presents a continuation of work at the National Bureau of Standards on 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], and sulfuric acid [4]. The evaluation procedures have been described [2,3,5] in substantial detail and a bibliography [6] giving the results 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. 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 symbols used throughout this paper. In general, we have attempted to adhere to the recommendations of the IUPAC [7] with regard to nomenclature and units.

2. Osmotic Coefficients from Vapor Pressure Osmometry

To date in our evaluations we have considered activity and osmotic coefficient data based upon direct and indirect vapor pressure measurements, freezing point depression measurements, electromotive force measurements with and without transference and diffusion measurements. In 1963 Burge [8] proposed the use of a "thermoelectric differential vapor pressure method", first described by A. V. Hill [9], for the measurement of osmotic coefficients; this method has subsequently been known as vapor pressure osmometry. The use of this method has been described by Burge [8]: "Two thermistor beads forming two arms of a Wheatstone bridge are suspended in a saturated solvent atmosphere in a chamber whose temperature is very carefully controlled. The bridge is balanced with solvent drops on both beads, and then the solvent on one bead is replaced by a drop of solution. Condensation from the saturated atmosphere warms the bead thus changing its resistance and unbalancing the bridge. The experimentally observed quantity is the amount of resistance change required to re-balance the bridge, which can be related to the temperature change of the bead". If the observed temperature difference is proportional to the chemical potential difference

($\Delta\mu$) between the pure solvent and the solvent in the solution, then it can be shown that

$$\Delta\mu = \frac{vM_1RTm\phi}{1000}$$

and

$$\phi = \frac{(\Delta\text{Res})}{vkm}$$

where m is the molality of the electrolyte solution, ϕ the osmotic coefficient, (ΔRes) is the difference in resistance between the thermistors, and k is an experimental calibration constant.

It should be noted that the measured change in resistance (which for small temperature differences is very nearly proportional to the temperature difference between the two thermistors) will be dependent not only upon the vapor pressure but also upon the transport properties of the solution under investigation. The method of vapor pressure osmometry should be valid if the transport properties of the solution under investigation and the solvent are the same. This ideal case is approached as the solution becomes more dilute. We are not aware of any detailed theoretical analysis that has been performed for the vapor pressure osmometer type experiment and, in the absence of such an analysis, we must look to the agreement (or lack of it) between measurements obtained with a vapor pressure osmometer and other more rigorous and established methods. The tests performed by Burge [8] using five different electrolyte solutions indicate a maximum difference of 0.012 and an average difference of 0.005 in the osmotic coefficient for eighteen different measurements at molalities up to 0.4 mol·kg⁻¹. For the compound [Co(NH₃)₅NO₂]Cl₂, Harkins, Hall, and Roberts [10] report freezing point depression data from which we have obtained osmotic coefficients at 25° C. Comparison of these results with the osmotic coefficients of Masterton and Scola [11] obtained with a vapor pressure osmometer show a difference of 0.022 in the osmotic coefficient at a molality of 0.01 mol·kg⁻¹. This difference is not unreasonable. Based upon these comparisons and also the fact that there are no other data available, we have decided to include in this compilation data for a series of cobalt compounds based upon the work of Masterton and Scola [11] and Berka and Masterton [12]. Insofar as the results for these systems are based upon a method that is not completely rigorous and since there are no comparison results on these systems, one must use these results with some degree of caution.

3. Evaluated Activity and Osmotic Coefficients

3.1. Presentation of Data

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

¹ Figures in brackets indicate literature references.

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 [13]. 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:

$$\phi = 1 + \frac{A_1}{B^2 I} \{- (1 + BI^{1/2}) + 2 \ln (1 + BI^{1/2}) \} \quad (1b)$$

$$+ 1/(1 + BI^{1/2}) \} + 1/2 Cm + 2/3 Dm^2 + 3/4 Em^3 + \dots,$$

$$\phi = 1 - \frac{A_1}{3} I^{1/2} - \frac{A_2}{2} I [\ln I + \frac{1}{2}] \\ + \sum_{i=1}^N B_i \frac{(i+1)}{(i+3)} m^{(i+1)/2}, \quad (2b)$$

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 $A_2 = \frac{2}{3} A^2 = 0.92238 \text{ mol}^{-1} \cdot \text{kg}$. 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 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.

4. A deviation plot in $\Delta\phi$ 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 $\Delta G^{\text{ex}} = G - G_{\text{ideal}} = \nu mRT (1 - \phi + \ln \gamma)$.

3.2. Sinusoidal Behavior Observed in the Fitting of Several Data Sets

While fitting several data sets (CoBr_2 , CoI_2 , $[\text{Co}(\text{NH}_3)_5 \text{CH}_3\text{CH}_2\text{COO}] \text{Br}_2$, $[\text{Co}(\text{NH}_3)_5 \text{CH}_3\text{CH}_2\text{COO}] \text{Cl}_2$, $[\text{Co}(\text{NH}_3)_5 \text{CH}_3\text{COO}] \text{Cl}_2$, $[\text{Co}(\text{NH}_3)_5 (\text{CH}_3)_2 \text{CHCOO}] (\text{NO}_3)_2$, $[\text{Co}(\text{NH}_3)_5 (\text{CH}_3)_2 \text{CHCOO}] \text{Cl}_2$, *trans*- $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2 \text{NH}_3\text{NO}_2] \text{Br}_2$, *trans*- $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2 \text{NH}_3\text{NO}_2] \text{Cl}_2$, and *cis*- $[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2 \text{NH}_3\text{NO}_2] \text{Cl}_2$ with the three different correlating equations, it was observed that there was a sinusoidal behavior in the deviation plots for these data sets. This phenomenon was observed using all three correlating equations and could not be eliminated by using any reasonable number of additional parameters. We note that this sinusoidal behavior is, in all cases, well within a reasonable assignment of the experimental accuracy of the measurements, and we do not believe that it is physically real. It is probably attributable to some artifact(s) inherent in the experimental procedures.

3.3. Supersaturated Solutions

For four systems considered herein (NiCl_2 , CoBr_2 , CoI_2 , and $\text{Co}(\text{NO}_3)_2$) the data apparently extend beyond the solubility limit and we have assumed that they pertain to reasonably stable supersaturated solutions. While the solubilities tabulated by Linke and Seidell [13] appear, with the exception of CoI_2 , to be reliable, the workers [37, 49, 51] who reported the isopiestic data made no mention of the solubilities or the stabilities of the solutions. We suggest that it would be desirable if future experimental work took more cognizance of these matters.

3.4. Evaluated Systems

FeCl₂Recommended Values for the mean activity and osmotic coefficient of FeCl₂ in H₂O at 298.15 K

| $m/mol \cdot kg^{-1}$ | γ | ϕ | a_w | $\Delta G^{ex}/J \cdot kg^{-1}$ |
|-----------------------|----------|--------|---------|---------------------------------|
| .001 | .8879 | .9619 | .999948 | -1. |
| .002 | .8496 | .9487 | .999897 | -2. |
| .003 | .8230 | .9394 | .999848 | -3. |
| .004 | .8020 | .9321 | .999799 | -5. |
| .005 | .7847 | .9261 | .999750 | -6. |
| .006 | .7698 | .9209 | .999701 | -8. |
| .007 | .7568 | .9164 | .999653 | -10. |
| .008 | .7452 | .9124 | .999606 | -12. |
| .009 | .7348 | .9088 | .999558 | -15. |
| .010 | .7252 | .9055 | .999511 | -17. |
| .020 | .6594 | .8835 | .999046 | -45. |
| .030 | .6196 | .8710 | .998589 | -78. |
| .040 | .5915 | .8630 | .998136 | -115. |
| .050 | .5702 | .8575 | .997685 | -156. |
| .060 | .5533 | .8537 | .997235 | -199. |
| .070 | .5394 | .8510 | .996785 | -244. |
| .080 | .5278 | .8493 | .996335 | -291. |
| .090 | .5179 | .8481 | .995883 | -339. |
| .100 | .5093 | .8475 | .995430 | -388. |
| .200 | .4625 | .8555 | .990796 | -932. |
| .300 | .4459 | .8740 | .985928 | -1521. |
| .400 | .4411 | .8964 | .980807 | -2127. |
| .500 | .4427 | .9208 | .975425 | -2735. |
| .600 | .4487 | .9463 | .969778 | -3336. |
| .700 | .4579 | .9728 | .963865 | -3925. |
| .800 | .4696 | 1.0000 | .957683 | -4497. |
| .900 | .4837 | 1.0279 | .951231 | -5049. |
| 1.000 | .4998 | 1.0564 | .944507 | -5577. |
| 1.250 | .5491 | 1.1300 | .926501 | -6781. |
| 1.500 | .6114 | 1.2070 | .906783 | -7797. |
| 1.750 | .6882 | 1.2874 | .885357 | -8604. |
| 2.000 | .7818 | 1.3712 | .862246 | -9181. |
| 2.050 | .8029 | 1.3883 | .857425 | -9268. |

| $m/mol \cdot kg^{-1}$ | $\sigma(\phi)$ | $\sigma(\Delta G^{ex})$ | $\sigma(\gamma)$ |
|-----------------------|----------------|-------------------------|------------------|
| .001 | .0002 | .0003 | .0003 |
| .010 | .0011 | .0024 | .0018 |
| .100 | .0035 | .0101 | .0052 |
| 1.000 | .0027 | .0124 | .0062 |
| 2.000 | .0040 | .0137 | .0107 |
| 2.050 | .0045 | .0142 | .0114 |

Coefficients of Correlating Equations

| | Eqs 1 | | Eqs 2 | | Eqs 3 | |
|-----|----------------|------------------|----------------|------------------|-----------------|------------------|
| Par | coefficient | σ (coeff) | coefficient | σ (coeff) | coefficient | σ (coeff) |
| 1 | .1454574343+01 | .611-01 | .2249978466+01 | .123+00 | .7437321432+01 | .275+00 |
| 2 | .4201237072+00 | .355-01 | .5129329559+01 | .186+00 | -.7056917492+01 | .681+00 |
| 3 | .4413168866-01 | .109-01 | .8714662847+00 | .712-01 | .3695358343+01 | .587+00 |
| 4 | | | | | -.7481810268+00 | .170+00 |

$$\begin{aligned}\sigma(\text{eqs 1}) &= .517-02 \\ \sigma(\text{eqs 2}) &= .888-02 \\ \sigma(\text{eqs 3}) &= .546-02\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

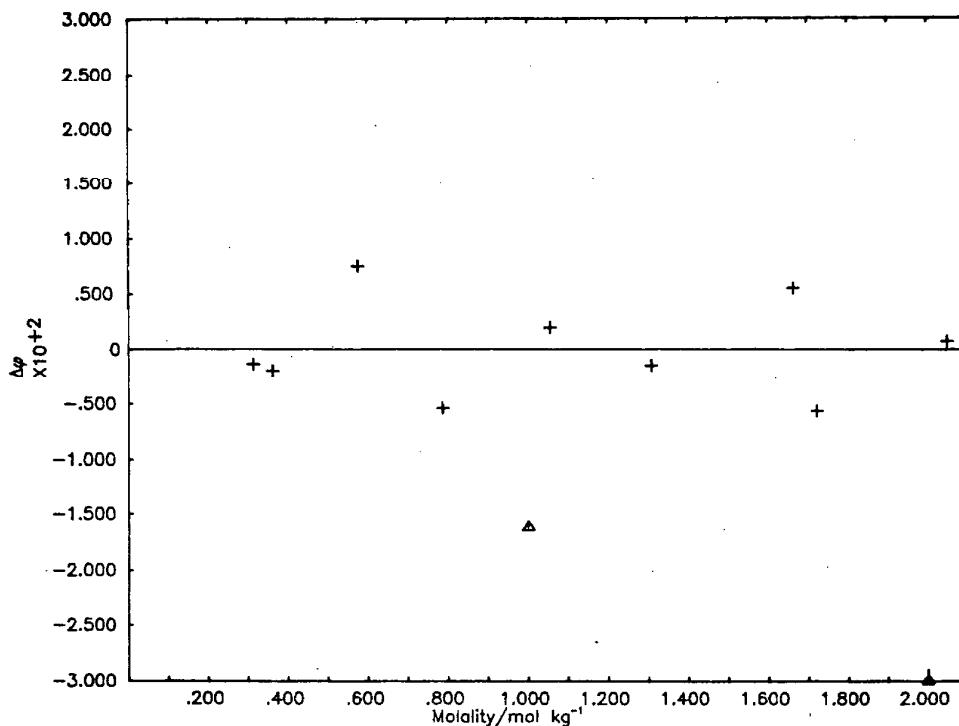
Kangro and Groeneveld [30]. Vapor pressure measurements. Assigned weight is zero.

Stokes and Robinson [31]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\vartheta_{298.15}$ | $m/\text{mol} \cdot \text{kg}^{-1}$ | $\vartheta_{298.15}$ |
|-------------------------------------|----------------------|-------------------------------------|----------------------|
| 1.000 | 1.0402 | •313200 | •8755 |
| 2.000 | 1.3401 | •362500 | •8858 |
| 3.000 | 1.6162 | •570000 | •9476 |
| 4.000 | 1.8015 | •787600 | •9912 |
| 5.000 | 1.9425 | 1.056000 | 1.0745 |
| | | 1.309000 | 1.1464 |
| | | 1.664000 | 1.2649 |
| | | 1.723000 | 1.2729 |
| | | 2.050000 | 1.3891 |

Comments

The isopiestic data of Stokes and Robinson [31] are preferred to the vapor pressure measurements of Kangro and Groeneveld [30] and the old freezing point depression measurements of Biltz [38].

Deviation Plot For FeCl_2 : $\Delta\vartheta$ vs molality

▲ Kangro and Groeneveld [30], vapor pressure

+ Stokes and Robinson [31], isopiestic vs KCl

NiCl_2 Recommended Values for the mean activity and osmotic coefficient of NiCl_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 | .8890 | .9626 | .999948 | -1. |
| .002 | .8517 | .9498 | .999897 | -2. |
| .003 | .8257 | .9410 | .999847 | -3. |
| .004 | .8055 | .9341 | .999798 | -4. |
| .005 | .7887 | .9285 | .999749 | -6. |
| .006 | .7744 | .9236 | .999701 | -8. |
| .007 | .7619 | .9194 | .999652 | -10. |
| .008 | .7508 | .9157 | .999604 | -12. |
| .009 | .7408 | .9124 | .999556 | -14. |
| .010 | .7317 | .9094 | .999509 | -16. |
| .020 | .6689 | .8895 | .999039 | -43. |
| .030 | .6312 | .8785 | .998577 | -76. |
| .040 | .6047 | .8715 | .998118 | -111. |
| .050 | .5845 | .8668 | .997660 | -150. |
| .060 | .5684 | .8636 | .997204 | -191. |
| .070 | .5553 | .8613 | .996747 | -234. |
| .080 | .5442 | .8599 | .996289 | -279. |
| .090 | .5348 | .8589 | .995831 | -324. |
| .100 | .5266 | .8585 | .995371 | -372. |
| .200 | .4818 | .8662 | .990681 | -887. |
| .300 | .4659 | .8837 | .985774 | -1445. |
| .400 | .4619 | .9056 | .980613 | -2017. |
| .500 | .4647 | .9303 | .975175 | -2590. |
| .600 | .4725 | .9571 | .969439 | -3154. |
| .700 | .4841 | .9858 | .963391 | -3703. |
| .800 | .4990 | 1.0161 | .957019 | -4232. |
| .900 | .5169 | 1.0477 | .950315 | -4736. |
| 1.000 | .5378 | 1.0805 | .943273 | -5212. |
| 1.250 | .6024 | 1.1670 | .924190 | -6263. |
| 1.500 | .6857 | 1.2580 | .903044 | -7087. |
| 1.750 | .7892 | 1.3517 | .879987 | -7659. |
| 2.000 | .9150 | 1.4466 | .855247 | -7963. |
| 2.250 | 1.0658 | 1.5411 | .829113 | -7987. |
| 2.500 | 1.2440 | 1.6338 | .801912 | -7725. |
| 2.750 | 1.4520 | 1.7238 | .773986 | -7175. |
| 3.000 | 1.6919 | 1.8100 | .745677 | -6339. |
| 3.250 | 1.9650 | 1.8915 | .717309 | -5221. |
| 3.500 | 2.2723 | 1.9679 | .689178 | -3830. |
| 3.750 | 2.6137 | 2.0387 | .661540 | -2173. |
| 4.000 | 2.9885 | 2.1035 | .634606 | -261. |
| 4.250 | 3.3950 | 2.1624 | .608540 | 1894. |
| 4.500 | 3.8315 | 2.2154 | .583453 | 4280. |
| 4.750 | 4.2955 | 2.2627 | .559410 | 6885. |
| 5.000 | 4.7854 | 2.3048 | .536423 | 9696. |
| 5.060(sat) | 4.9067 | 2.3142 | .531061 | 10400. |
| 5.250 | 5.3001 | 2.3424 | .514463 | 12703. |
| 5.500 | 5.8401 | 2.3762 | .493453 | 15894. |
| 5.714 | 6.3247 | 2.4028 | .476139 | 18766. |
| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln\gamma)$ | $\sigma(\gamma)$ | |
| .001 | .0001 | .0002 | .0002 | |
| .010 | .0006 | .0014 | .0011 | |
| .100 | .0019 | .0056 | .0030 | |
| 1.000 | .0014 | .0073 | .0039 | |
| 2.000 | .0010 | .0069 | .0063 | |
| 5.000 | .0017 | .0071 | .0338 | |
| 5.714 | .0036 | .0081 | .0514 | |

Coefficients of Correlating Equations

| Par | <u>Eqs 1</u> | | <u>Eqs 2</u> | | <u>Eqs 3</u> | |
|-----|-----------------|------------------|-----------------|------------------|-----------------|------------------|
| | coefficient | σ (coeff) | coefficient | σ (coeff) | coefficient | σ (coeff) |
| 1 | .1696340541+01 | .382-01 | .2070223884+01 | .395-01 | .8914750111+01 | .153+00 |
| 2 | .2467283620+00 | .193-01 | .5615103283+01 | .590-01 | .1155991114+02 | .483+00 |
| 3 | .2060360886+00 | .973-02 | -.1263167631+01 | .311-01 | .9401176965+01 | .630+00 |
| 4 | -.4083972677-01 | .216-02 | .1189064951+00 | .554-02 | .4201470999+01 | .460+00 |
| 5 | .2383360533-02 | .169-03 | | | .9595911444+00 | .128+00 |
| 6 | | | | | -.8868857702-01 | .158-01 |

$$\begin{aligned}\sigma(\text{eqs 1}) &= .371-02 \\ \sigma(\text{eqs 2}) &= .454-02 \\ \sigma(\text{eqs 3}) &= .372-02\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Dieterici [32]. Vapor pressure measurements at 0°C. Assigned weight is zero. These measurements were adjusted to 25°C using the Φ_L and Φ_C data given for NiCl_2 in the table of auxiliary data.

Robinson and Stokes [35]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\Phi_{298.15}$ | $m/\text{mol} \cdot \text{kg}^{-1}$ | $\Phi_{298.15}$ |
|-------------------------------------|-----------------|-------------------------------------|-----------------|
| .004000 | 1.0410 | .116800 | .8549 |
| 2.060000 | 1.3620 | .197500 | .8638 |
| 2.576000 | 1.7520 | .215800 | .8712 |
| | | .538000 | .9434 |
| | | .786400 | 1.0145 |
| | | .943000 | 1.0638 |
| | | 1.212000 | 1.1535 |
| | | 1.443000 | 1.2372 |
| | | 1.831000 | 1.3823 |
| | | 2.123000 | 1.4962 |

Jones et al. [33]. Freezing point depression measurements. Assigned weight is zero.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\Phi_{298.15}$ | $m/\text{mol} \cdot \text{kg}^{-1}$ | $\Phi_{298.15}$ |
|-------------------------------------|-----------------|-------------------------------------|-----------------|
| .037000 | .9856 | 1.052100 | 1.0904 |
| .074100 | .9098 | 1.245300 | 1.1590 |
| .149300 | .9102 | 1.407200 | 1.2243 |
| .223800 | .9234 | 1.573500 | 1.2758 |
| .298400 | .9368 | 1.931400 | 1.4346 |
| .374300 | .9563 | 2.047400 | 1.4619 |
| .449400 | .9622 | 2.143700 | 1.5044 |
| .525700 | .9844 | 2.374400 | 1.5850 |
| .753200 | 1.0574 | 2.503000 | 1.6366 |
| .812000 | 1.0510 | 2.695300 | 1.7165 |
| .915600 | 1.0944 | 2.765300 | 1.7531 |
| 1.019700 | 1.1239 | | |
| 1.548600 | 1.3183 | | |
| 2.093500 | 1.5926 | | |
| 2.656600 | 1.8993 | | |
| 3.240100 | 1.9369 | | |
| 3.825500 | 2.0056 | | |

Shul'ts et al. [36]. Isopiestic measurements, reference salt is NaCl. Assigned weight is 0.2.

Pearce and Eckstrom [34]. Vapor pressure measurements. Assigned weight is zero.

Shul'ts et al. [36]. Isopiestic measurements, reference salt is KCl. Assigned weight is 0.2.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\Phi_{298.15}$ | $m/\text{mol} \cdot \text{kg}^{-1}$ | $\Phi_{298.15}$ |
|-------------------------------------|-----------------|-------------------------------------|-----------------|
| .100000 | .8169 | 1.052100 | 1.0863 |
| .200000 | .8281 | 1.245300 | 1.1542 |
| .400000 | .8648 | 1.407200 | 1.2213 |
| .600000 | .9087 | 1.573500 | 1.2788 |
| .800000 | .9598 | 1.931400 | 1.4234 |
| 1.000000 | 1.0167 | | |
| 1.500000 | 1.1742 | | |
| 2.000000 | 1.3422 | | |
| 2.500000 | 1.5176 | | |
| 3.000000 | 1.6969 | | |
| 4.000000 | 2.0643 | | |
| 4.911600 | 2.4032 | | |

Shul'ts et al. [36].
Isopiestic measurements,
reference salt is CaCl_2 .
Assigned weight is 0.2.

$m/\text{mol} \cdot \text{kg}^{-1}$

$\vartheta_{298.15}$

| | |
|----------|--------|
| 2.503000 | 1.6238 |
| 2.695300 | 1.7004 |
| 2.765300 | 1.7367 |
| 2.843000 | 1.7547 |
| 3.101400 | 1.8382 |
| 3.519300 | 1.9768 |
| 3.937500 | 2.0765 |
| 4.321700 | 2.1697 |
| 4.539500 | 2.2147 |
| 4.920300 | 2.2914 |

Shul'ts et al. [36]. Iso-
piestic measurements, reference
salt is NH_4Cl . Assigned weight
is 0.2.

$m/\text{mol} \cdot \text{kg}^{-1}$

$\vartheta_{298.15}$

| | |
|----------|--------|
| 1.052100 | 1.0940 |
| 1.245300 | 1.1773 |
| 1.447200 | 1.2353 |
| 1.573500 | 1.2922 |
| 1.931400 | 1.4274 |
| 2.047400 | 1.4706 |
| 2.143700 | 1.5085 |
| 2.374400 | 1.5892 |
| 2.503000 | 1.6339 |
| 2.695300 | 1.7130 |
| 2.765300 | 1.7460 |

Stokes [37]. Isopiestic
measurements, reference salt
is CaCl_2 . Assigned weight is
1.0.

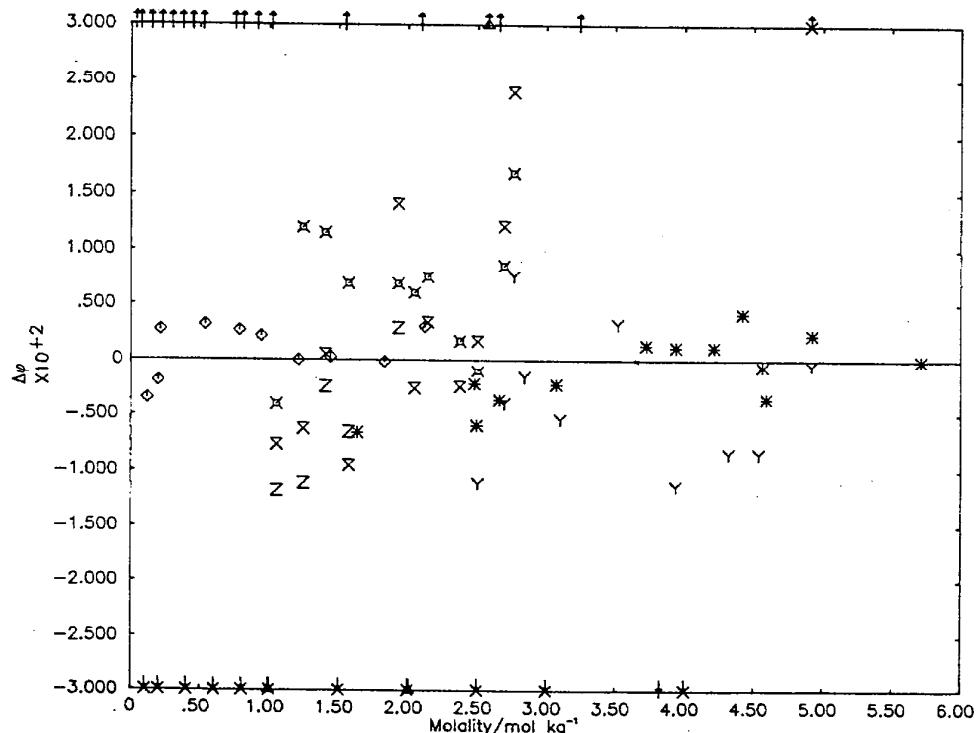
$m/\text{mol} \cdot \text{kg}^{-1}$

$\vartheta_{298.15}$

| | |
|----------|--------|
| 1.634000 | 1.3014 |
| 2.479000 | 1.6239 |
| 2.456000 | 1.6264 |
| 2.660000 | 1.6881 |
| 3.073000 | 1.8320 |
| 3.725000 | 2.0332 |
| 3.941000 | 2.0899 |
| 4.217000 | 2.1561 |
| 4.422000 | 2.2036 |
| 4.567000 | 2.2279 |
| 4.595000 | 2.2304 |
| 4.926000 | 2.2951 |
| 5.714000 | 2.4028 |

Comments

The most reliable data for this system appear to be the isopiestic data of Robinson and Stokes [35] and of Stokes [37] which are more precise than the isopiestic data of Shul'ts et al. [36], which are, nevertheless, in good agreement with the results of the former workers. The freezing point depression measurements of Jones et al. [33] and of Biltz [38] are not very accurate and were given zero weight. Again, trusting the isopiestic data, we have given zero weight to the vapor pressure measurements of Pearce and Eckstrom [34] and of Dieterici [32]. The emf measurements of Hass and Jellineck [39] involve unknown liquid junction potentials and cannot be treated rigorously.



Deviation Plot For NiCl_2 : $\Delta\vartheta$ vs molality

▲ Dieterici, [32], vapor pressure

● Shul'ts et al. [36], isopiestic vs KCl

+ Jones et al. [33], freezing point depression

Y Shul'ts et al. [36], isopiestic vs CaCl_2

X Pearce and Eckstrom [34], vapor pressure

☒ Shul'ts et al. [36], isopiestic vs NH_4Cl

◊ Robinson and Stokes [35], isopiestic vs KCl

* Stokes [37], isopiestic vs CaCl_2

✗ Shul'ts et al. [36], isopiestic vs NaCl

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

| <i>m/mol·kg⁻¹</i> | <i>γ</i> | <i>φ</i> | <i>a_w</i> | <i>ΔG^{ex}/J·kg⁻¹</i> |
|------------------------------|----------|----------|----------------------|--|
| .001 | .8911 | .9637 | .999948 | -1. |
| .002 | .8555 | .9520 | .999897 | -2. |
| .003 | .8310 | .9440 | .999847 | -3. |
| .004 | .8121 | .9380 | .999797 | -4. |
| .005 | .7966 | .9331 | .999748 | -6. |
| .006 | .7835 | .9290 | .999699 | -8. |
| .007 | .7721 | .9256 | .999650 | -10. |
| .008 | .7620 | .9225 | .999601 | -12. |
| .009 | .7529 | .9199 | .999553 | -14. |
| .010 | .7447 | .9175 | .999504 | -16. |
| .020 | .6898 | .9032 | .999024 | -41. |
| .030 | .6581 | .8968 | .998547 | -70. |
| .040 | .6367 | .8939 | .998069 | -103. |
| .050 | .6211 | .8929 | .997590 | -137. |
| .060 | .6092 | .8931 | .997108 | -173. |
| .070 | .5999 | .8941 | .996623 | -211. |
| .080 | .5925 | .8957 | .996135 | -249. |
| .090 | .5866 | .8978 | .995643 | -289. |
| .100 | .5817 | .9002 | .995147 | -329. |
| .200 | .5666 | .9335 | .989960 | -746. |
| .300 | .5789 | .9743 | .984327 | -1162. |
| .400 | .6042 | 1.0186 | .978220 | -1554. |
| .500 | .6391 | 1.0656 | .971615 | -1908. |
| .600 | .6825 | 1.1149 | .964492 | -2217. |
| .700 | .7342 | 1.1664 | .956833 | -2475. |
| .800 | .7947 | 1.2199 | .948621 | -2675. |
| .900 | .8649 | 1.2754 | .939846 | -2815. |
| 1.000 | .9458 | 1.3329 | .930497 | -2890. |
| 1.250 | 1.2045 | 1.4843 | .904585 | -2773. |
| 1.500 | 1.5689 | 1.6462 | .875064 | -2184. |
| 1.750 | 2.0833 | 1.8174 | .842070 | -1086. |
| 2.000 | 2.8125 | 1.9968 | .805668 | 555. |
| 2.250 | 3.8519 | 2.1832 | .766838 | 2768. |
| 2.500 | 5.3407 | 2.3754 | .725459 | 5577. |
| 2.750 | 7.4822 | 2.5723 | .682284 | 9004. |
| 3.000 | 10.5726 | 2.7726 | .637915 | 13066. |
| 3.250 | 15.0408 | 2.9753 | .592974 | 17777. |
| 3.500 | 21.5051 | 3.1789 | .548079 | 23149. |
| 3.501 | 21.5454 | 3.1800 | .547847 | 23178. |

| <i>m/mol·kg⁻¹</i> | <i>σ(φ)</i> | <i>σ(lnγ)</i> | <i>σ(γ)</i> |
|------------------------------|-------------|---------------|-------------|
| .001 | .0001 | .0003 | .0003 |
| .010 | .0008 | .0019 | .0014 |
| .100 | .0021 | .0066 | .0038 |
| 1.000 | .0015 | .0074 | .0070 |
| 2.000 | .0022 | .0078 | .0220 |
| 3.501 | .0045 | .0084 | .1816 |

Coefficients of Correlating Equations

| | Eqs 1 | | Eqs 2 | | Eqs 3 | |
|-----|-----------------|----------|-----------------|----------|-----------------|----------|
| Par | coefficient | σ(coeff) | coefficient | σ(coeff) | coefficient | σ(coeff) |
| 1 | .2034414594+01 | .534-01 | .2535082534+01 | .156+00 | .1161235347+02 | .322+00 |
| 2 | .6564378817+00 | .219-01 | .6357417713+01 | .456+00 | -.1943715100+02 | .131+01 |
| 3 | .2059946779+00 | .114-01 | -.2618148959+01 | .521+00 | .2144353725+02 | .221+01 |
| 4 | -.1746069568-01 | .193-02 | .9705194801+00 | .264+00 | -.1360468076+02 | .183+01 |
| 5 | | | -.1677338781+00 | .493-01 | .4639229414+01 | .744+00 |
| 6 | | | | | -.6546251526+00 | .118+00 |

$$\begin{aligned}\sigma(\text{eqs 1}) &= .508-02 \\ \sigma(\text{eqs 2}) &= .493-02 \\ \sigma(\text{eqs 3}) &= .478-02\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Libus and Sadowska [40].
Isopiestic measurements,
reference salt is KCl. Assigned
weight is 1.0.

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\vartheta_{298.15}$ |
|-----------------------------------|----------------------|
| .098100 | .8936 |
| .103600 | .9012 |
| .181800 | .9289 |
| .195900 | .9357 |
| .357800 | .9995 |
| .425500 | 1.0304 |
| .538200 | 1.0840 |
| .568300 | 1.0965 |
| .585500 | 1.1047 |
| .739000 | 1.1855 |
| .766500 | 1.2055 |
| .892000 | 1.2736 |
| .960700 | 1.3084 |
| .985500 | 1.3276 |
| 1.222100 | 1.4699 |
| 1.235300 | 1.4782 |
| 1.297400 | 1.5117 |
| 1.325300 | 1.5365 |
| 1.449700 | 1.6199 |
| 1.556200 | 1.6854 |

Libus and Sadowska [41],
isopiestic measurements,
reference salt is $\text{Mg}(\text{ClO}_4)_2$.
Assigned weight is 1.0.

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\vartheta_{298.15}$ |
|-----------------------------------|----------------------|
| 2.363800 | 2.2750 |
| 2.794700 | 2.6136 |
| 3.145300 | 2.8909 |
| 3.501300 | 3.1774 |

Libus and Sadowska [40],
isopiestic measurements, ref-
erence salt is NaClO_4 . Assigned
weight is 1.0.

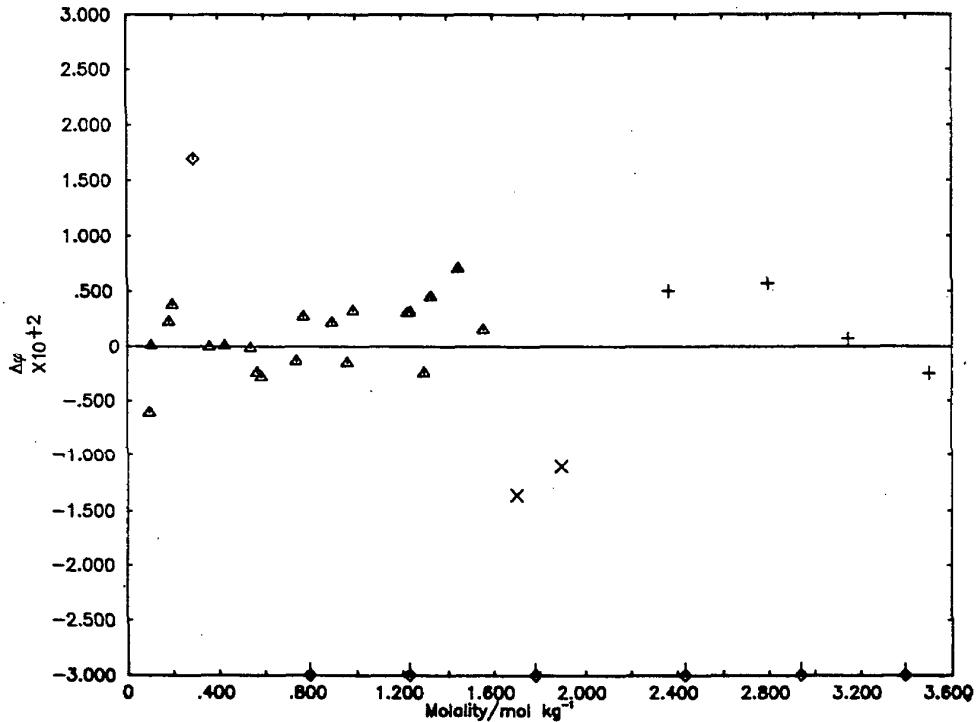
| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\vartheta_{298.15}$ |
|-----------------------------------|----------------------|
| 1.701500 | 1.7699 |
| 1.895200 | 1.9096 |

Lilich and Andreev [41].
Vapor pressure measurements.
Assigned weight is zero.

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\vartheta_{298.15}$ |
|-----------------------------------|----------------------|
| .291000 | .9874 |
| .794000 | 1.1345 |
| 1.229000 | 1.4244 |
| 1.781000 | 1.7670 |
| 2.434000 | 2.2446 |
| 2.938000 | 2.6081 |
| 3.394000 | 2.9470 |

Comments

We prefer the isopiestic measurements of Libus and Sadowska [40] over the vapor pressure measurements of Lilich and Andreev [41].

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

▲ Libus and Sadowska [40], isopiestic vs KCl

+ Libus and Sadowska [40], isopiestic vs $\text{Mg}(\text{ClO}_4)_2$ X Libus and Sadowska [40], isopiestic vs NaClO_4

◆ Lilich and Andreev [41], vapor pressure

NiBr₂Recommended Values for the mean activity and osmotic coefficient of NiBr₂ in H₂O at 298.15 K

| $m/mol \cdot kg^{-1}$ | γ | ϕ | a_w | $\Delta G^{ex}/J \cdot kg^{-1}$ |
|-----------------------|----------|--------|---------|---------------------------------|
| .001 | .8895 | .9628 | .999948 | -1. |
| .002 | .8526 | .9504 | .999897 | -2. |
| .003 | .8271 | .9418 | .999847 | -3. |
| .004 | .8072 | .9352 | .999798 | -4. |
| .005 | .7909 | .9298 | .999749 | -6. |
| .006 | .7769 | .9252 | .999700 | -8. |
| .007 | .7647 | .9212 | .999652 | -10. |
| .008 | .7539 | .9177 | .999603 | -12. |
| .009 | .7442 | .9146 | .999555 | -14. |
| .010 | .7354 | .9118 | .999507 | -16. |
| .020 | .6752 | .8938 | .999034 | -43. |
| .030 | .6396 | .8846 | .998567 | -74. |
| .040 | .6149 | .8793 | .998101 | -109. |
| .050 | .5965 | .8762 | .997635 | -146. |
| .060 | .5821 | .8745 | .997168 | -185. |
| .070 | .5705 | .8738 | .996700 | -226. |
| .080 | .5610 | .8738 | .996229 | -269. |
| .090 | .5530 | .8743 | .995756 | -312. |
| .100 | .5463 | .8752 | .995281 | -357. |
| .200 | .5144 | .8961 | .990360 | -834. |
| .300 | .5108 | .9257 | .985102 | -1333. |
| .400 | .5192 | .9590 | .979481 | -1828. |
| .500 | .5352 | .9946 | .973480 | -2305. |
| .600 | .5569 | 1.0321 | .967086 | -2755. |
| .700 | .5836 | 1.0711 | .960289 | -3173. |
| .800 | .6151 | 1.1115 | .953080 | -3555. |
| .900 | .6513 | 1.1532 | .945453 | -3895. |
| 1.000 | .6924 | 1.1961 | .937403 | -4192. |
| 1.250 | .8188 | 1.3080 | .915423 | -4722. |
| 1.500 | .9846 | 1.4259 | .890834 | -4925. |
| 1.750 | 1.1994 | 1.5485 | .863761 | -4772. |
| 2.000 | 1.4763 | 1.6747 | .834414 | -4242. |
| 2.250 | 1.8315 | 1.8034 | .803078 | -3318. |
| 2.500 | 2.2854 | 1.9335 | .770095 | -1988. |
| 2.750 | 2.8628 | 2.0637 | .735858 | -243. |
| 3.000 | 3.5936 | 2.1929 | .700783 | 1924. |
| 3.250 | 4.5121 | 2.3200 | .665305 | 4514. |
| 3.500 | 5.6571 | 2.4438 | .629854 | 7526. |
| 3.750 | 7.0702 | 2.5630 | .594842 | 10956. |
| 4.000 | 8.7935 | 2.6766 | .560656 | 14796. |
| 4.250 | 10.8661 | 2.7834 | .527645 | 19036. |
| 4.500 | 13.3180 | 2.8821 | .496116 | 23661. |
| 4.693 | 15.4806 | 2.9520 | .472957 | 27486. |

| $m/mol \cdot kg^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln\gamma)$ | $\sigma(\gamma)$ |
|-----------------------|----------------|---------------------|------------------|
| .001 | .0001 | .0001 | .0001 |
| .010 | .0004 | .0008 | .0006 |
| .100 | .0011 | .0031 | .0017 |
| 1.000 | .0008 | .0041 | .0028 |
| 2.000 | .0009 | .0038 | .0056 |
| 4.693 | .0027 | .0045 | .0696 |

Coefficients of Correlating Equations

| <u>Eqs 1</u> | | <u>Eqs 2</u> | | <u>Eqs 3</u> | |
|--------------|--------------------|-----------------------------------|--------------------|-----------------------------------|--------------------|
| <u>Par</u> | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> |
| 1 | .1754027013+01 | .210-01 | .18391124594+01 | .160+00 | .9609761265+01 |
| 2 | .5102956934+00 | .857-02 | .7512801735+01 | .558+00 | -.1308178632+02 |
| 3 | .1481756515+00 | .321-02 | -.40136416554+01 | .799+00 | .1158014343+02 |
| 4 | -.1697362496-01 | .399-03 | .19272386584+01 | .568+00 | -.5830112806+01 |
| 5 | | | -.54727027264+00 | .198+00 | .1572972292+01 |
| 6 | | | .6228601921-01 | .271-01 | -.1787678878+00 |

$$\begin{aligned}\sigma(\text{eqs 1}) &= .341-02 \\ \sigma(\text{eqs 2}) &= .335-02 \\ \sigma(\text{eqs 3}) &= .403-02\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

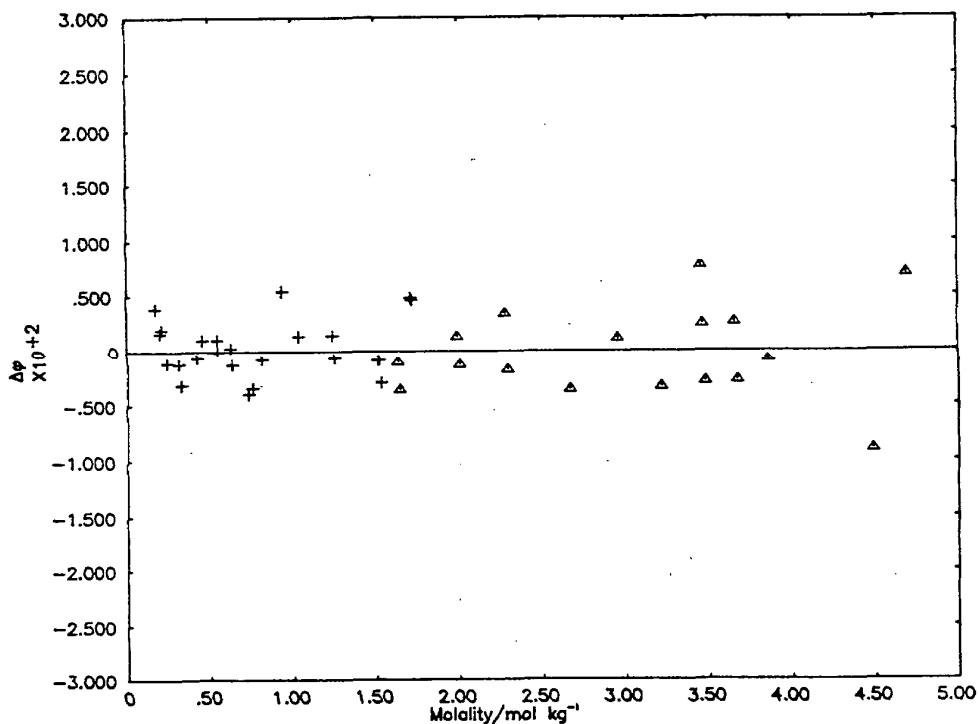
Libus et al. [50a]. Isopiestic measurements, reference salt is $\text{Mg}(\text{ClO}_4)_2$. Assigned weight is 1.0.

Libus et al. [50a]. Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

| $m_{\text{ref}}/\text{mol}\cdot\text{kg}^{-1}$ | $m/\text{mol}\cdot\text{kg}^{-1}$ | $\theta_{298.15}$ | $m_{\text{ref}}/\text{mol}\cdot\text{kg}^{-1}$ | $m/\text{mol}\cdot\text{kg}^{-1}$ | $\theta_{298.15}$ |
|--|-----------------------------------|-------------------|--|-----------------------------------|-------------------|
| 1.499 | 1.631000 | 1.4885 | 0.2595 | .175900 | .8938 |
| 1.509 | 1.644000 | 1.4924 | 0.3101 | .208100 | .9000 |
| 1.821 | 1.994000 | 1.6730 | 0.3194 | .213800 | .9019 |
| 1.828 | 2.004000 | 1.6754 | 0.3626 | .241000 | .9065 |
| 2.073 | 2.281000 | 1.8229 | 0.4860 | .314000 | .9290 |
| 2.080 | 2.293000 | 1.8239 | 0.516 | .331800 | .9329 |
| 2.403 | 2.669000 | 2.0179 | 0.689 | .426300 | .9675 |
| 2.653 | 2.959000 | 2.1730 | 0.761 | .463500 | .9825 |
| 2.865 | 3.215000 | 2.2990 | 0.933 | .551000 | 1.0135 |
| 3.074 | 3.458000 | 2.4309 | 0.934 | .551000 | 1.0146 |
| 3.077 | 3.466000 | 2.4296 | 1.104 | .633000 | 1.0451 |
| 3.084 | 3.479000 | 2.4306 | 1.113 | .638000 | 1.0454 |
| 3.235 | 3.659000 | 2.5228 | 1.325 | .736000 | 1.0815 |
| 3.241 | 3.671000 | 2.5231 | 1.371 | .756000 | 1.0901 |
| 3.394 | 3.859000 | 2.6125 | 1.511 | .815000 | 1.1168 |
| 3.630 | 4.485000 | 2.8674 | 1.834 | .944000 | 1.1773 |
| 3.876 | 4.693000 | 2.9589 | 2.085 | 1.044000 | 1.2167 |
| | | | 2.635 | 1.245000 | 1.3072 |
| | | | 2.648 | 1.251000 | 1.3078 |
| | | | 3.418 | 1.510000 | 1.4298 |
| | | | 3.446 | 1.519000 | 1.4342 |
| | | | 3.485 | 1.533000 | 1.4389 |
| | | | 4.084 | 1.715000 | 1.5359 |
| | | | 4.100 | 1.720000 | 1.5382 |

Comments

In a recent, careful study, Libus et al. [50a] performed isopiestic measurements on NiBr_2 . Unfortunately, in their data tables, there exists an erroneous setting of the columns for the data for NiBr_2 and CuBr_2 . The correct [50b] experimental data for this system is given above along with the calculated osmotic coefficients.



Deviation Plot for NiBr_2 : $\Delta\Phi$ vs molality

- ▲ Libus et al. [50a], isopiestic vs $\text{Mg}(\text{ClO}_4)_2$
- + Libus et al. [50a], isopiestic vs KCl

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

| <i>m/mol·kg⁻¹</i> | <i>γ</i> | <i>φ</i> | <i>a_w</i> | <i>ΔG^{ex}/J·kg⁻¹</i> |
|------------------------------|----------|----------|----------------------|--|
| .001 | .8886 | .9623 | .999948 | -1. |
| .002 | .8510 | .9495 | .999857 | -2. |
| .003 | .8248 | .9405 | .999848 | -3. |
| .004 | .8043 | .9335 | .999798 | -4. |
| .005 | .7874 | .9277 | .999749 | -6. |
| .006 | .7729 | .9228 | .999701 | -8. |
| .007 | .7603 | .9185 | .999653 | -10. |
| .008 | .7490 | .9147 | .999605 | -12. |
| .009 | .7389 | .9113 | .999557 | -14. |
| .010 | .7297 | .9083 | .999509 | -17. |
| .020 | .6662 | .8879 | .999041 | -44. |
| .030 | .6281 | .8768 | .998579 | -76. |
| .040 | .6015 | .8699 | .998121 | -113. |
| .050 | .5813 | .8653 | .997664 | -152. |
| .060 | .5653 | .8623 | .997208 | -193. |
| .070 | .5522 | .8603 | .996751 | -230. |
| .080 | .5413 | .8591 | .996293 | -281. |
| .090 | .5321 | .8585 | .995833 | -328. |
| .100 | .5241 | .8583 | .995372 | -375. |
| .200 | .4814 | .8691 | .990649 | -893. |
| .300 | .4672 | .8888 | .985692 | -1450. |
| .400 | .4643 | .9114 | .980489 | -2019. |
| .500 | .4675 | .9354 | .975039 | -2587. |
| .600 | .4746 | .9602 | .969343 | -3148. |
| .700 | .4847 | .9855 | .963401 | -3694. |
| .800 | .4973 | 1.0113 | .957216 | -4224. |
| .900 | .5119 | 1.0375 | .950788 | -4733. |
| 1.000 | .5284 | 1.0639 | .944120 | -5219. |
| 1.250 | .5777 | 1.1316 | .926403 | -6324. |
| 1.500 | .6382 | 1.2011 | .907215 | -7253. |
| 1.750 | .7110 | 1.2727 | .886589 | -7989. |
| 2.000 | .7975 | 1.3463 | .864570 | -8517. |
| 2.250 | .8998 | 1.4219 | .841210 | -8826. |
| 2.500 | 1.0209 | 1.4997 | .816578 | -8906. |
| 2.750 | 1.1641 | 1.5796 | .790751 | -8746. |
| 3.000 | 1.3337 | 1.6617 | .763820 | -8338. |
| 3.250 | 1.5349 | 1.7459 | .735889 | -7673. |
| 3.500 | 1.7743 | 1.8324 | .707070 | -6742. |
| 3.750 | 2.0597 | 1.9211 | .677487 | -5538. |
| 4.000 | 2.4010 | 2.0121 | .647273 | -4053. |
| 4.250 | 2.8101 | 2.1053 | .616568 | -2279. |
| 4.500 | 3.3022 | 2.2008 | .585519 | -208. |
| 4.623 | 3.5802 | 2.2486 | .570163 | .921. |

| <i>m/mol·kg⁻¹</i> | <i>σ(φ)</i> | <i>σ(lnγ)</i> | <i>σ(γ)</i> |
|------------------------------|-------------|---------------|-------------|
| .001 | .0003 | .0006 | .0005 |
| .010 | .0019 | .0042 | .0030 |
| .100 | .0063 | .0177 | .0093 |
| 1.000 | .0044 | .0271 | .0143 |
| 2.000 | .0053 | .0240 | .0191 |
| 4.623 | .0392 | .0621 | .2225 |

Coefficients of Correlating Equations

| <u>Eqs 1</u> | | <u>Eqs 2</u> | | <u>Eqs 3</u> | | |
|--------------|--------------------|-----------------------------------|--------------------|-----------------------------------|--------------------|-----------------------------------|
| <u>Par</u> | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> | <u>σ(coeff)</u> |
| 1 | .1592802472+01 | .103+00 | .2834408378+01 | .813-01 | .7720545072+01 | .238+00 |
| 2 | .4177466957+00 | .355-01 | .4331827343+01 | .968-01 | .7270364465+01 | .472+00 |
| 3 | .2845173944-01 | .751-02 | .5906189949+00 | .307-01 | .3598839648+01 | .323+00 |
| 4 | | | | | .6719760416-00 | .743-01 |

$$\begin{aligned}\sigma(\text{eqs 1}) &= .159-01 \\ \sigma(\text{eqs 2}) &= .153-01 \\ \sigma(\text{eqs 3}) &= .130-01\end{aligned}$$

Experimental Data Employed in Generation of Correlation Equations

Dieterici [32]. Vapor pressure measurements.
Assigned weight is zero.

$$\begin{array}{ll}m/\text{mol} \cdot \text{kg}^{-1} & \vartheta_{298.15} \\ \hline 1.001000 & .8680 \\ 1.969000 & 1.1000\end{array}$$

Frolov et al. [42]. Isopiestic measurements,
reference salt was not specified by these workers.
Assigned weight is zero.

$$\begin{array}{ll}m/\text{mol} \cdot \text{kg}^{-1} & \vartheta_{298.15} \\ \hline .740000 & 1.0210 \\ .856200 & 1.0220 \\ 1.050000 & 1.0600 \\ 1.229600 & 1.0550 \\ 1.291000 & 1.1470 \\ 1.597000 & 1.1260 \\ 1.875000 & 1.1830 \\ 2.553000 & 1.3430 \\ 2.707000 & 1.3900 \\ 3.838000 & 1.6690\end{array}$$

Jones et al. [33]. Freezing point depression
measurements. ϑ_L and ϑ_C data for NiCl_2 were used
in treating these measurements. Assigned weight
is zero.

$$\begin{array}{ll}m/\text{mol} \cdot \text{kg}^{-1} & \vartheta_{298.15} \\ \hline .076300 & .8755 \\ .153100 & .8661 \\ .308000 & .8732\end{array}$$

Jones and Pearce [43]. Freezing point depression
measurements. Assigned weight is zero.

$$\begin{array}{ll}m/\text{mol} \cdot \text{kg}^{-1} & \vartheta_{298.15} \\ \hline .010050 & .9762 \\ .025025 & .9239 \\ .050096 & .8816 \\ .075213 & .8637 \\ .100380 & .8753 \\ .252420 & .8740\end{array}$$

King et al. [14]. Freezing point depression
measurements. Assigned weight is zero.

$$\begin{array}{ll}m/\text{mol} \cdot \text{kg}^{-1} & \vartheta_{298.15} \\ \hline .050000 & .9453 \\ .075000 & .9274 \\ .100000 & .9217 \\ .125000 & .9180 \\ .150000 & .9130 \\ .175000 & .9011 \\ .200000 & .8903 \\ .225000 & .8897 \\ .250000 & .8884 \\ .275000 & .8906 \\ .300000 & .8935\end{array}$$

Ryabov et al. [44]. Isopiestic measurements,
reference salt was not specified by these workers.
Assigned weight is 1.0.

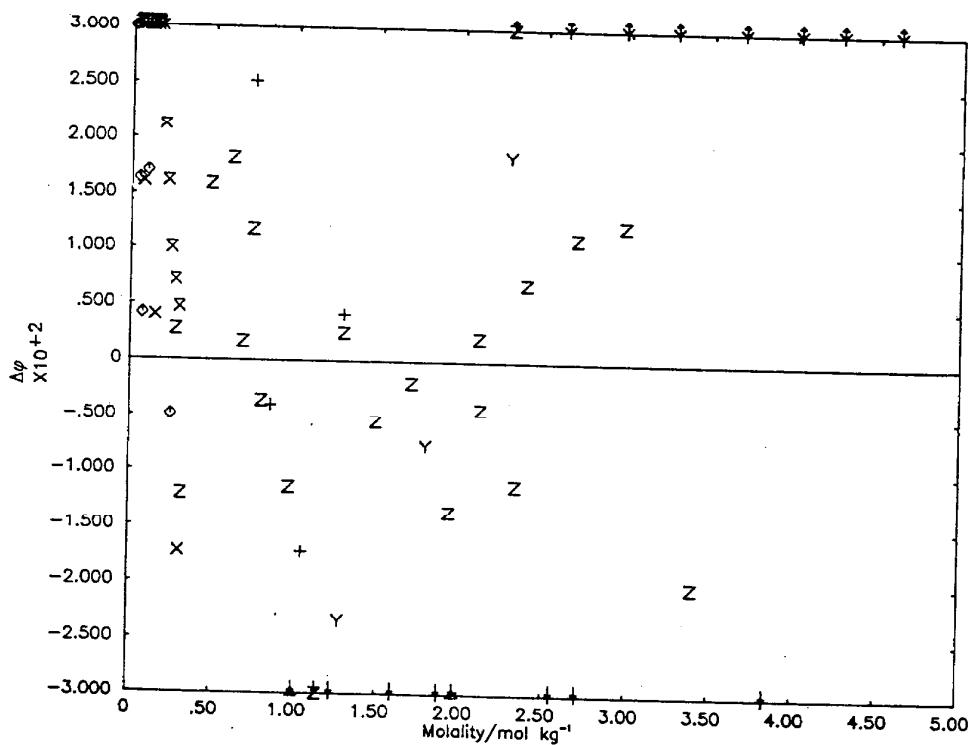
$$\begin{array}{ll}m/\text{mol} \cdot \text{kg}^{-1} & \vartheta_{298.15} \\ \hline .278600 & .8870 \\ .319200 & .8809 \\ .485500 & .9478 \\ .615800 & .9824 \\ .684600 & .9833 \\ .746000 & 1.0075 \\ .799200 & 1.0075 \\ .970600 & 1.0447 \\ 1.144800 & 1.04681 \\ 1.250800 & 1.1453 \\ 1.489600 & 1.1927 \\ 1.701700 & 1.2568 \\ 1.933900 & 1.3130 \\ 2.107600 & 1.3807 \\ 2.118500 & 1.3776 \\ 2.292900 & 1.4698 \\ 2.332000 & 1.4360 \\ 2.390300 & 1.4723 \\ 2.691600 & 1.45718 \\ 2.981300 & 1.4677 \\ 3.398000 & 1.7767\end{array}$$

Yakimov and Guzhavina [45]. Vapor pressure measurements. Assigned weight is zero.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\Delta\phi$ |
|-------------------------------------|--------------|
| | 298.15 |
| 4.623000 | 2.4008 |
| 4.276000 | 2.2605 |
| 4.020000 | 2.1353 |
| 3.685000 | 2.0099 |
| 3.277000 | 1.8867 |
| 2.969000 | 1.7674 |
| 2.622000 | 1.6065 |
| 2.284000 | 1.4509 |
| 1.787000 | 1.2758 |
| 1.274000 | 1.1148 |

Comments

There is an unusually large amount of scatter for $\text{Ni}(\text{NO}_3)_2$ system and we have relied entirely on the isopiestic results of Ryabov et al [44], who, unfortunately neither gave their experimental measurements nor did they state the reference electrolyte they used. The vapor pressure data of Yakimov and Guzhavina [45] scatter about the isopiestic data as do most of the freezing point depression data [33,43,14]. A more carefully documented isopiestic investigation would be of value here.



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

- ▲ Dieterici [32], vapor pressure
- + Frolov et al. [42], isopiestic vs ?
- ✗ Jones et al. [33], freezing point depression
- ◊ Jones and Pearce [43], freezing point depression
- ✗ King et al. [14], freezing point depression
- Z Ryabov et al. [44], isopiestic vs ?
- Y Yakimov and Guzhavina [45], vapor pressure

CoCl₂Recommended Values for the mean activity and osmotic coefficient of CoCl₂ in H₂O at 298.15 K

| <i>m/mol·kg</i> ⁻¹ | <i>Y</i> | <i>φ</i> | <i>a_w</i> | <i>ΔG^{ex}/J·kg</i> ⁻¹ |
|-------------------------------|----------|----------|----------------------|---|
| .001 | .8891 | .9626 | .999948 | -1. |
| .002 | .8519 | .9500 | .999897 | -2. |
| .003 | .8260 | .9412 | .999847 | -3. |
| .004 | .8059 | .9343 | .999798 | -4. |
| .005 | .7892 | .9287 | .999749 | -6. |
| .006 | .7750 | .9239 | .999700 | -8. |
| .007 | .7625 | .9198 | .999652 | -10. |
| .008 | .7514 | .9161 | .999604 | -12. |
| .009 | .7415 | .9128 | .999556 | -14. |
| .010 | .7324 | .9098 | .999508 | -16. |
| .020 | .6700 | .8901 | .999038 | -43. |
| .030 | .6325 | .8793 | .998575 | -75. |
| .040 | .6061 | .8724 | .998116 | -111. |
| .050 | .5860 | .8677 | .997658 | -150. |
| .060 | .5700 | .8645 | .997200 | -190. |
| .070 | .5569 | .8623 | .996743 | -233. |
| .080 | .5459 | .8608 | .996285 | -277. |
| .090 | .5365 | .8599 | .995826 | -323. |
| .100 | .5284 | .8594 | .995366 | -370. |
| .200 | .4834 | .8666 | .990676 | -883. |
| .300 | .4671 | .8834 | .985778 | -1438. |
| .400 | .4626 | .9044 | .980638 | -2009. |
| .500 | .4648 | .9281 | .975232 | -2581. |
| .600 | .4718 | .9538 | .969544 | -3146. |
| .700 | .4824 | .9812 | .963560 | -3697. |
| .800 | .4962 | 1.0100 | .957270 | -4229. |
| .900 | .5128 | 1.0400 | .950671 | -4738. |
| 1.000 | .5320 | 1.0710 | .943759 | -5221. |
| 1.250 | .5912 | 1.1519 | .925128 | -6299. |
| 1.500 | .6659 | 1.2359 | .904662 | -7167. |
| 1.750 | .7566 | 1.3209 | .882560 | -7806. |
| 2.000 | .8639 | 1.4051 | .859093 | -8201. |
| 2.250 | .9882 | 1.4670 | .834581 | -8348. |
| 2.500 | 1.1295 | 1.5663 | .809368 | -8246. |
| 2.750 | 1.2877 | 1.6390 | .783799 | -7897. |
| 3.000 | 1.4617 | 1.7072 | .758203 | -7308. |
| 3.250 | 1.6501 | 1.7693 | .732874 | -6489. |
| 3.500 | 1.8508 | 1.8250 | .708064 | -5450. |
| 3.750 | 2.0614 | 1.8741 | .683973 | -4204. |
| 4.000 | 2.2794 | 1.9168 | .660743 | -2765. |
| 4.118 | 2.3840 | 1.9348 | .659111 | -2023. |

| <i>m/mol·kg</i> ⁻¹ | <i>σ(φ)</i> | <i>σ(lny)</i> | <i>σ(Y)</i> |
|-------------------------------|-------------|---------------|-------------|
| .001 | .0002 | .0004 | .0003 |
| .010 | .0011 | .0025 | .0018 |
| .100 | .0029 | .0090 | .0048 |
| 1.000 | .0021 | .0097 | .0052 |
| 2.000 | .0022 | .0103 | .0089 |
| 4.118 | .0058 | .0120 | .0287 |

Coefficients of Correlating Equations

| | Eqs 1 | | | Eqs 2 | | |
|-----|-----------------|----------|-----------------|----------|-----------------|----------|
| Par | coefficient | σ(coeff) | coefficient | σ(coeff) | coefficient | σ(coeff) |
| 1 | .1724803367+01 | .696-01 | .2034073132+01 | .773-01 | .8835017198+01 | .181+00 |
| 2 | .2257683320+00 | .471-01 | .5710716949+01 | .142+01 | -.1102415691+02 | .486+00 |
| 3 | .2103460579+00 | .328-01 | -.1349883870+01 | .911-01 | .8190289847+01 | .507+00 |
| 4 | -.4852062356-01 | .103-01 | .1344546927+00 | .196-01 | -.3023801793+01 | .235+00 |
| 5 | .3238217201-02 | .113-02 | | | .4298568295+00 | .402-01 |

$$\begin{aligned} \sigma(\text{eqs 1}) &= .875-02 \\ \sigma(\text{eqs 2}) &= .997-02 \\ \sigma(\text{eqs 3}) &= .948-02 \end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Isopiestic data of Downes [20]. Reference salt is CaCl_2 . Assigned weight is 1.0.

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\varnothing_{298.15}$ |
|-----------------------------------|------------------------|
| 1.534600 | 1.2483 |
| 1.815300 | 1.3412 |
| 2.181700 | 1.4621 |
| 2.762000 | 1.6425 |
| 3.018000 | 1.7198 |
| 3.223800 | 1.7682 |
| 3.384800 | 1.8120 |
| 3.451000 | 1.8243 |
| 3.790300 | 1.8952 |
| 4.117900 | 1.9606 |

Isopiestic data of Robinson [48]. Reference salt is KCl. Assigned weight is 1.0.

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\varnothing_{298.15}$ |
|-----------------------------------|------------------------|
| .058710 | .8438 |
| .128400 | .8446 |
| .224600 | .8643 |
| .341200 | .8946 |
| .415000 | .9086 |
| .501100 | .9298 |
| .572900 | .9450 |
| .632000 | .9617 |
| .684600 | .9796 |
| .810600 | 1.0106 |
| .903400 | 1.0369 |
| 1.057000 | 1.0830 |
| 1.106000 | 1.1013 |
| 1.303000 | 1.1753 |
| 1.416000 | 1.2070 |
| 1.500000 | 1.2288 |
| 1.612000 | 1.2769 |
| 1.718000 | 1.3138 |
| 2.084000 | 1.4560 |

Isopiestic data of Downes [20]. Reference salt is NaCl. Assigned weight is 1.0.

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\varnothing_{298.15}$ |
|-----------------------------------|------------------------|
| .609800 | .9547 |
| .668000 | .9707 |
| .746500 | .9926 |
| 1.336600 | 1.1776 |
| 1.539300 | 1.2448 |
| 1.634900 | 1.2790 |
| 1.754800 | 1.3352 |
| 1.592800 | 1.3985 |
| 2.429100 | 1.5478 |

Isopiestic data of Robinson and Brown [49]. Reference salt is CaCl_2 . Assigned weight is 1.0.

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\varnothing_{298.15}$ |
|-----------------------------------|------------------------|
| .335100 | .8895 |
| .349200 | .8930 |
| .839800 | 1.0225 |
| 1.033000 | 1.0844 |
| 1.235000 | 1.1505 |
| 1.543000 | 1.2543 |
| 1.570000 | 1.3931 |
| 2.081000 | 1.4306 |
| 2.170000 | 1.4564 |
| 2.473000 | 1.5452 |
| 2.754000 | 1.6385 |
| 2.794000 | 1.6538 |
| 2.898000 | 1.6736 |
| 3.512000 | 1.8104 |
| 3.687000 | 1.8544 |
| 3.878000 | 1.8773 |
| 4.064000 | 1.9073 |

Freezing point depression data of Hall and Harkins [46]. Assigned weight is 1.0.

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\varnothing_{298.15}$ |
|-----------------------------------|------------------------|
| .001730 | .9626 |
| .002090 | .9508 |
| .008620 | .9155 |
| .010080 | .9116 |
| .022510 | .8886 |
| .023750 | .8891 |
| .054750 | .8687 |
| .059730 | .8680 |
| .125600 | .8639 |
| .277200 | .8938 |
| .421700 | .9239 |

Freezing point depression data of Jones and Getman [47]. Assigned weight is zero.

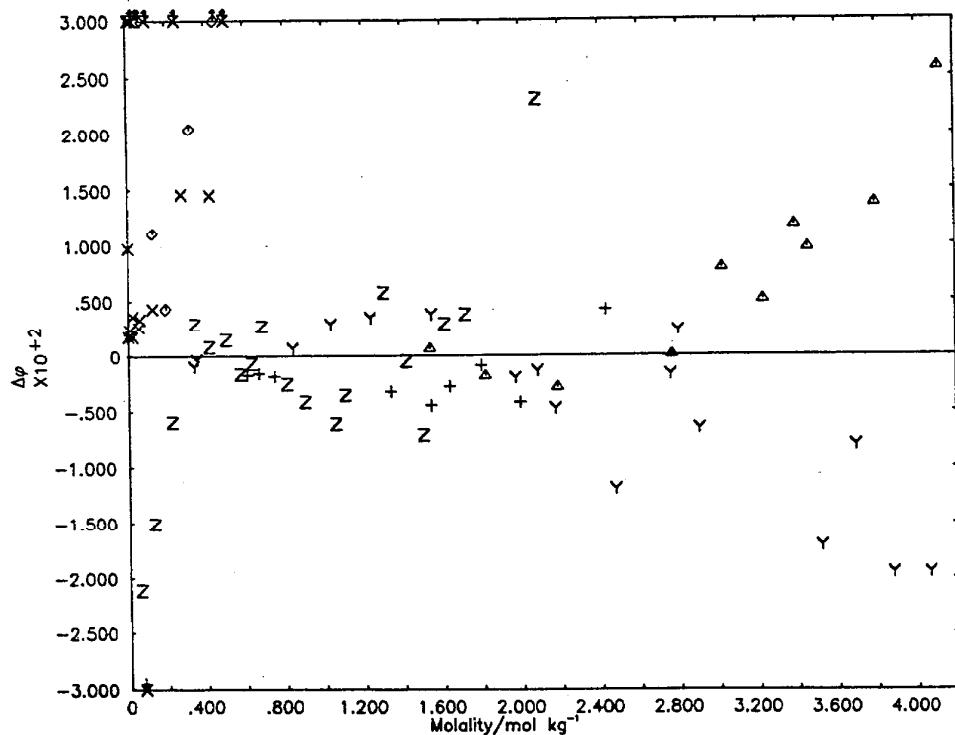
| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\varnothing_{298.15}$ |
|-----------------------------------|------------------------|
| .063960 | .8993 |
| .128200 | .8708 |
| .192800 | .8700 |
| .321400 | .9081 |
| .450900 | .9573 |

Freezing point depression data of Jones and Pearce [43]. Assigned weight is zero.

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\varnothing_{298.15}$ |
|-----------------------------------|------------------------|
| .010003 | 1.1142 |
| .025010 | .9913 |
| .050040 | .9239 |
| .075090 | .7893 |
| .100150 | .9026 |
| .251000 | .9235 |
| .504300 | .9994 |

Comments

For CoCl_2 , freezing point depression measurements have been reported by Biltz [38], Hall and Harkins [48], Jones et al [33], Jones and Getman [47], and Jones and Pearce [43]. The old results of Biltz [38] are totally unreasonable and are not given above. The data sets of Jones and Getman [47] and Jones et al [33] appear to be identical, but none of Jones' results were given any weight. Only the careful measurements of Hall and Harkins [46], which were found to merge well with the isopiestic data, were found to be of any value from these various data sets based on freezing point depression measurements. It should be noted that the various isopiestic measurements, based on these different reference salts, are in good agreement up to about 2.5 $\text{mol}\cdot\text{kg}^{-1}$, but that at greater molalities the more recent results of Downes [20] differ systematically from the earlier results of Robinson and Brown [49]. Downes [20] has noted that this systematic difference may be attributable, in part, to experimental difficulties with the analyses of the stock solutions. We have weighted equally the results of Downes [20] and of Robinson and Brown [49]. It should be noted that the freezing point depression data of Hall and Harkins [46], even though given unit weight, differ systematically from our final fit. This is attributable to two constraints imposed during the fitting process: (a) that the limiting slope be given by Debye-Hückel theory and (b) the large amount of isopiestic data that also must be accommodated.

Deviation Plot For CoCl_2 : $\Delta\theta$ vs molality

- ▲ Downes [20], isopiestic vs CaCl_2
- + Downes [20], isopiestic vs NaCl
- X Hall and Harkins [46], freezing point depression
- ◇ Jones and Getman [47], freezing point depression
- ✗ Jones and Pearce [43], freezing point depression
- Z Robinson [48], isopiestic vs KCl
- Y Robinson and Brown [49], isopiestic vs CaCl_2

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

| <u>m/mol·kg⁻¹</u> | <u>Y</u> | <u>φ</u> | <u>a₂₀</u> | <u>ΔG^{ex}/J·kg⁻¹</u> |
|------------------------------|-------------|---------------|-----------------------|--|
| .001 | .8913 | .9638 | .99948 | -1. |
| .002 | .8558 | .9521 | .99897 | -2. |
| .003 | .8315 | .9443 | .99847 | -3. |
| .004 | .8127 | .9363 | .99797 | -4. |
| .005 | .7973 | .9335 | .99748 | -6. |
| .006 | .7843 | .9295 | .99699 | -8. |
| .007 | .7729 | .9261 | .99650 | -10. |
| .008 | .7629 | .9231 | .99601 | -12. |
| .009 | .7539 | .9205 | .99552 | -14. |
| .010 | .7458 | .9182 | .99504 | -16. |
| .020 | .6914 | .9042 | .99023 | -41. |
| .030 | .6602 | .8981 | .998545 | -70. |
| .040 | .6391 | .8954 | .998066 | -102. |
| .050 | .6238 | .8946 | .997585 | -136. |
| .060 | .6122 | .8950 | .997102 | -172. |
| .070 | .6031 | .8962 | .996615 | -209. |
| .080 | .5959 | .8979 | .996125 | -247. |
| .090 | .5901 | .9001 | .995631 | -286. |
| .100 | .5855 | .9020 | .995134 | -326. |
| .200 | .5719 | .9368 | .989925 | -737. |
| .300 | .5855 | .9783 | .984264 | -1146. |
| .400 | .6123 | 1.0232 | .978123 | -1528. |
| .500 | .6487 | 1.0707 | .971480 | -1872. |
| .600 | .6938 | 1.1206 | .964315 | -2169. |
| .700 | .7474 | 1.1725 | .956610 | -2414. |
| .800 | .8101 | 1.2265 | .948350 | -2601. |
| .900 | .8827 | 1.2825 | .939524 | -2726. |
| 1.000 | .9663 | 1.3403 | .930125 | -2785. |
| 1.250 | 1.2336 | 1.4924 | .904094 | -2626. |
| 1.500 | 1.6094 | 1.6544 | .874484 | -1991. |
| 1.750 | 2.1386 | 1.8251 | .841458 | -845. |
| 2.000 | 2.8863 | 2.0032 | .805309 | 845. |
| 2.250 | 3.9468 | 2.1874 | .766445 | 3105. |
| 2.500 | 5.4560 | 2.3763 | .725366 | 5957. |
| 2.750 | 7.6087 | 2.5687 | .682643 | 9419. |
| 3.000 | 10.6829 | 2.7633 | .638885 | 13507. |
| 3.250 | 15.0710 | 2.9585 | .594718 | 18230. |
| 3.500 | 21.3221 | 3.1532 | .550752 | 23595. |
| 3.514 | 21.7566 | 3.1645 | .548220 | 23926. |
| <u>m/mol·kg⁻¹</u> | <u>σ(φ)</u> | <u>σ(lny)</u> | <u>σ(Y)</u> | |
| .001 | .0001 | .0003 | .0003 | |
| .010 | .0009 | .0020 | .0015 | |
| .100 | .0022 | .0071 | .0041 | |
| 1.000 | .0016 | .0082 | .0079 | |
| 2.000 | .0020 | .0083 | .0239 | |
| 3.514 | .0048 | .0092 | .1991 | |

Coefficients of Correlating Equations

| Par | Eqs 1 | | Eqs 2 | | Eqs 3 | |
|-----|-----------------|----------|-----------------|----------|-----------------|----------|
| | coefficient | σ(coeff) | coefficient | σ(coeff) | coefficient | σ(coeff) |
| 1 | .2069877024+01 | .573-01 | .2744591642+01 | .167+00 | .1374348933+02 | .868+00 |
| 2 | .6650962889+00 | .216-01 | .5798858975+01 | .486+00 | -.3096638506+02 | .462+01 |
| 3 | .2088219562+00 | .109-01 | -.1988615659+01 | .554+00 | .4788305655+02 | .103+02 |
| 4 | -.1952381040-01 | .182-02 | .6558508463+00 | .281+00 | -.4529889078+02 | .120+02 |
| 5 | | | -.1113246387+00 | .526-01 | .2541915831+02 | .768+01 |
| 6 | | | | | -.7711748831+01 | .254+01 |
| 7 | | | | | .9705587929+00 | .342+00 |

$$\begin{aligned} \sigma(\text{eqs 1}) &= .517-02 \\ \sigma(\text{eqs 2}) &= .527-02 \\ \sigma(\text{eqs 3}) &= .496-02 \end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Libus and Sadowska [40], isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\phi_{298.15}$ |
|-------------------------------------|-----------------|
| .097200 | .9019 |
| .110400 | .9043 |
| .182000 | .9279 |
| .195100 | .9396 |
| .424100 | 1.0338 |
| .566400 | 1.1001 |
| .582800 | 1.1098 |
| .736400 | 1.1897 |
| .765300 | 1.2106 |
| .910400 | 1.2904 |
| .957000 | 1.3134 |
| .981100 | 1.3335 |
| 1.075800 | 1.3676 |
| 1.217800 | 1.4751 |
| 1.293900 | 1.5158 |
| 1.321200 | 1.5412 |
| 1.476000 | 1.6455 |

Libus and Sadowska [40], isopiestic measurements, reference salt is $\text{Mg}(\text{ClO}_4)_2$. Assigned weight is 1.0.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\phi_{298.15}$ |
|-------------------------------------|-----------------|
| 2.187700 | 2.1613 |
| 2.410400 | 2.3302 |
| 2.706700 | 2.6289 |
| 3.057200 | 2.8245 |
| 3.514500 | 3.1819 |

Libus and Sadowska [40], isopiestic measurements, reference salt is NaClO_4 . Assigned weight is 1.0.

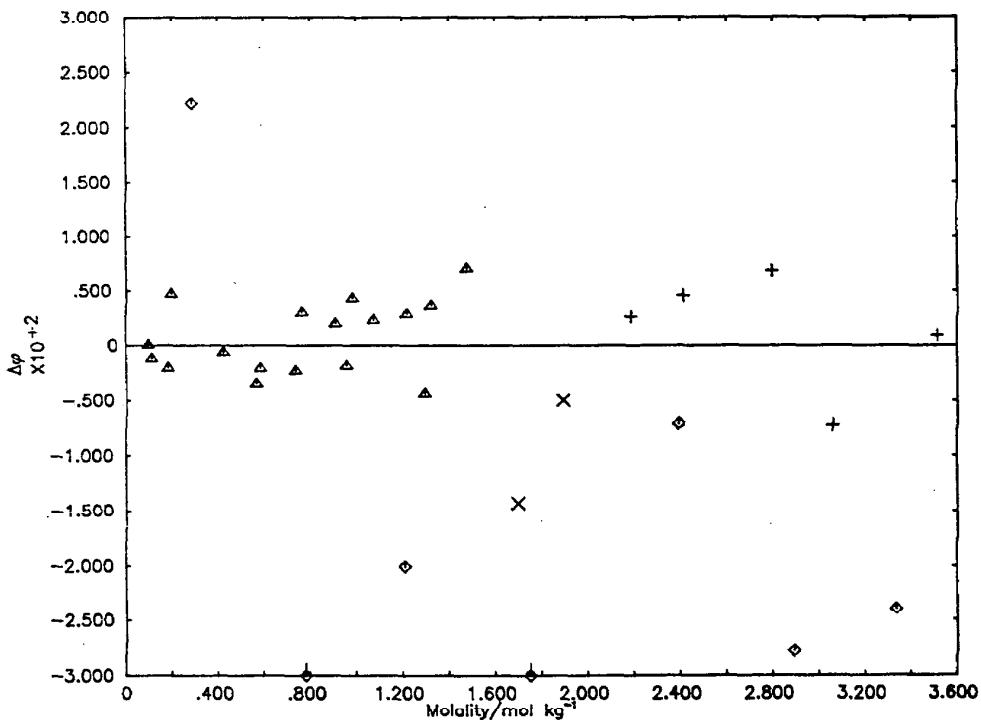
| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\phi_{298.15}$ |
|-------------------------------------|-----------------|
| 1.696300 | 1.7735 |
| 1.891500 | 1.9201 |
| 2.888000 | .9956 |
| 2.782000 | 1.1529 |
| 2.210000 | 1.4473 |
| 1.752000 | 1.7958 |
| 2.390000 | 2.2856 |
| 2.891000 | 2.6505 |
| 3.334000 | 3.0002 |

Lilich and Andreev [41]. Vapor pressure measurements. Assigned weight is zero.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\phi_{298.15}$ |
|-------------------------------------|-----------------|
| | |
| | |
| | |
| | |

Comments

We prefer the isopiestic measurements of Libus and Sadowska [40] over the vapor pressure measurements of Lilich and Andreev [41].



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

▲ Libus and Sadowska [40], isopiestic vs KCl

× Libus and Sadowska [40], isopiestic vs NaClO_4

+ Libus and Sadowska [40], isopiestic vs $\text{Mg}(\text{ClO}_4)_2$

◊ Lilich and Andreev [41], vapor pressure

CoBr_2 Recommended Values for the mean activity and osmotic coefficient of CoBr_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 | .8904 | .9633 | .999948 | -1. |
| .002 | .8541 | .9512 | .999897 | -2. |
| .003 | .8291 | .9429 | .999847 | -3. |
| .004 | .8097 | .9365 | .999798 | -4. |
| .005 | .7937 | .9314 | .999748 | -6. |
| .006 | .7801 | .9270 | .999699 | -8. |
| .007 | .7683 | .9232 | .999651 | -10. |
| .008 | .7578 | .9199 | .999602 | -12. |
| .009 | .7483 | .9170 | .999554 | -14. |
| .010 | .7398 | .9144 | .999506 | -16. |
| .020 | .6815 | .8976 | .999030 | -42. |
| .030 | .6471 | .8891 | .998559 | -72. |
| .040 | .6233 | .8842 | .998090 | -106. |
| .050 | .6054 | .8813 | .997621 | -142. |
| .060 | .5914 | .8797 | .997151 | -181. |
| .070 | .5801 | .8790 | .996680 | -220. |
| .080 | .5707 | .8789 | .996207 | -262. |
| .090 | .5629 | .8793 | .995732 | -304. |
| .100 | .5562 | .8800 | .995255 | -347. |
| .200 | .5235 | .8979 | .990341 | -811. |
| .300 | .5181 | .9241 | .985129 | -1298. |
| .400 | .5244 | .9541 | .979585 | -1783. |
| .500 | .5383 | .9869 | .973682 | -2254. |
| .600 | .5579 | 1.0220 | .967401 | -2702. |
| .700 | .5826 | 1.0591 | .960723 | -3121. |
| .800 | .6120 | 1.0980 | .953636 | -3504. |
| .900 | .6461 | 1.1384 | .946132 | -3850. |
| 1.000 | .6851 | 1.1802 | .938204 | -4153. |
| 1.250 | .8054 | 1.2901 | .916535 | -4709. |
| 1.500 | .9628 | 1.4056 | .892301 | -4948. |
| 1.750 | 1.1650 | 1.5248 | .865701 | -4842. |
| 2.000 | 1.4214 | 1.6458 | .837029 | -4375. |
| 2.250 | 1.7435 | 1.7669 | .806650 | -3532. |
| 2.500 | 2.1441 | 1.8867 | .774973 | -2306. |
| 2.750 | 2.6377 | 2.0039 | .742423 | -695. |
| 3.000 | 3.2402 | 2.1174 | .709419 | 1300. |
| 3.250 | 3.9679 | 2.2262 | .676355 | 3674. |
| 3.500 | 4.8378 | 2.3297 | .643587 | 6422. |
| 3.750 | 5.8665 | 2.4274 | .611417 | 9533. |
| 4.000 | 7.0703 | 2.5190 | .580092 | 12997. |
| 4.250 | 8.4647 | 2.6043 | .549800 | 16802. |
| 4.500 | 10.0648 | 2.6835 | .520667 | 20935. |
| 4.750 | 11.8861 | 2.7568 | .492764 | 25383. |
| 5.000 | 13.9461 | 2.8248 | .466107 | 30135. |
| 5.250 | 16.2662 | 2.8881 | .440665 | 35178. |
| 5.445(sat) | 18.2746 | 2.9348 | .421618 | 39308. |
| 5.500 | 18.8753 | 2.9476 | .416365 | 40503. |
| 5.672 | 20.8589 | 2.9870 | .400254 | 44325. |

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\sigma(\phi)$ | $\sigma(4w\gamma)$ | $\sigma(\gamma)$ |
|-----------------------------------|----------------|--------------------|------------------|
| .001 | .0004 | .0009 | .0008 |
| .010 | .0025 | .0056 | .0042 |
| .100 | .0065 | .0202 | .0112 |
| 1.000 | .0049 | .0220 | .0151 |
| 2.000 | .0044 | .0215 | .0306 |
| 5.000 | .0080 | .0217 | .3024 |
| 5.672 | .0160 | .0289 | .6026 |

Coefficients of Correlating Equations

| Par | <u>Eqs 1</u> | | <u>Eqs 2</u> | | <u>Eqs 3</u> | |
|-----|--------------------|-----------------------------------|--------------------|-----------------------------------|--------------------|-----------------------------------|
| | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> | <u>σ(coeff)</u> |
| 1 | .1937945402+01 | .159+00 | .2498602848+01 | .990-01 | .8642748306+01 | .254+00 |
| 2 | .3606771568+00 | .715-01 | .5255313068+01 | .158+00 | -.9636782913+01 | .599+00 |
| 3 | .2399520593+00 | .382-01 | -.1067261033+01 | .877-01 | .6489740636+01 | .543+00 |
| 4 | -.4623972375-01 | .885-02 | .8385252431-01 | .163-01 | -.2138147480+01 | .217+00 |
| 5 | .2694683656-02 | .717-03 | | | .2678063229+00 | .320-01 |

$$\begin{aligned}\sigma(\text{eqs 1}) &= .168-01 \\ \sigma(\text{eqs 2}) &= .172-01 \\ \sigma(\text{eqs 3}) &= .170-01\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Libus et al. [50a]. Reference salt is KCl.
Assigned weight is 1.0.

Robinson, McCoach and Lim [51]. Reference
electrolyte is CaBr₂. Assigned weight is 1.0.

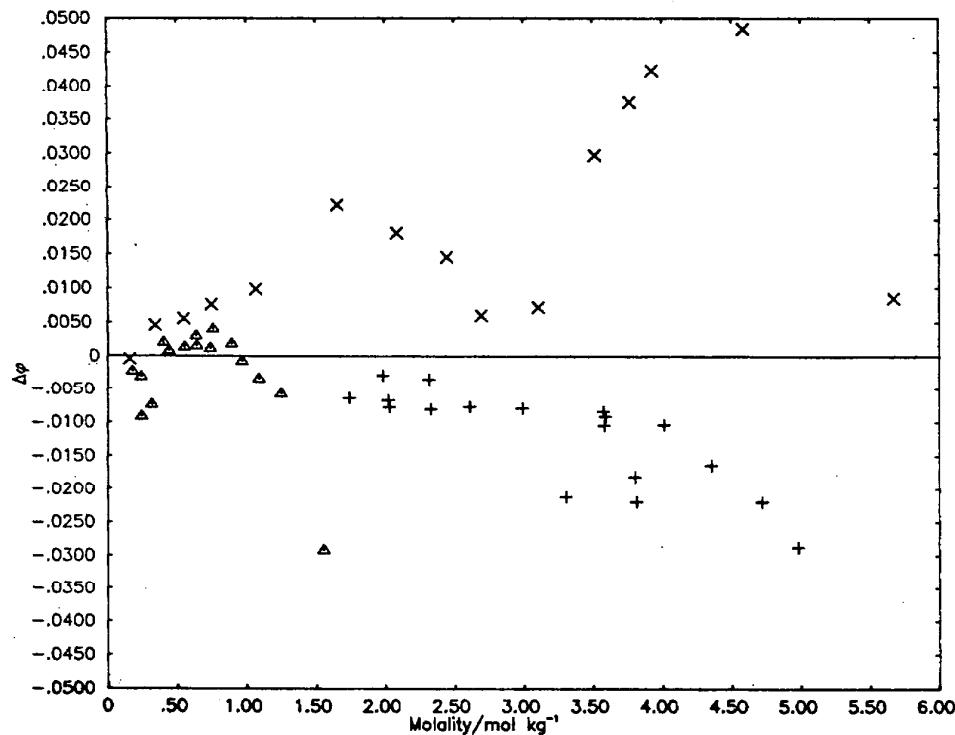
| <u>$m/\text{mol}\cdot\text{kg}^{-1}$</u> | <u>$\varnothing_{298.15}$</u> | <u>$m/\text{mol}\cdot\text{kg}^{-1}$</u> | <u>$\varnothing_{298.15}$</u> |
|---|--|---|--|
| .179000 | .8909 | .150300 | .8887 |
| .241400 | .9050 | .343500 | .9413 |
| .244700 | .8998 | .550300 | 1.0099 |
| .317700 | .9217 | .749100 | 1.0856 |
| .403500 | .9572 | 1.068000 | 1.2193 |
| .442500 | .9685 | 1.658000 | 1.5028 |
| .555000 | 1.0073 | 2.085000 | 1.7051 |
| .637000 | 1.0385 | 2.446000 | 1.8756 |
| .642000 | 1.0389 | 2.694000 | 1.9840 |
| .740000 | 1.0756 | 3.107000 | 2.1718 |
| .759000 | 1.0858 | 3.516000 | 2.3659 |
| .893000 | 1.1373 | 3.768000 | 2.4717 |
| .967000 | 1.1655 | 3.930000 | 2.5363 |
| 1.089000 | 1.2152 | 4.589000 | 2.7586 |
| 1.248000 | 1.2834 | 5.672000 | 2.9955 |
| 1.554000 | 1.4019 | | |

Libus et al. [50a]. Reference salt is Mg(ClO₄)₂.
Assigned weight is 1.0.

| <u>$m/\text{mol}\cdot\text{kg}^{-1}$</u> | <u>$\varnothing_{298.15}$</u> |
|---|--|
| 1.741000 | 1.5141 |
| 1.983000 | 1.6347 |
| 2.022000 | 1.6498 |
| 2.031000 | 1.6531 |
| 2.316000 | 1.7953 |
| 2.328000 | 1.7965 |
| 2.608000 | 1.9301 |
| 2.989000 | 2.1046 |
| 3.306000 | 2.2287 |
| 3.575000 | 2.3513 |
| 3.581000 | 2.3516 |
| 3.589000 | 2.3561 |
| 3.801000 | 2.4286 |
| 3.813000 | 2.4292 |
| 4.012000 | 2.5129 |
| 4.352000 | 2.6210 |
| 4.718000 | 2.7258 |
| 4.977000 | 2.7900 |

Comments

There is a fair amount of scatter in the data for this system. A part of it may be attributable to the uncertainties in the data for the reference salts, particularly in the data for CaBr_2 , the reference salt used by Robinson et al. [51].



Deviation Plot for CoBr_2 : $\Delta\phi$ vs molality

- Δ Libus et al. [50a], isopiestic vs KCl
- $+$ Libus et al. [50a], isopiestic vs $\text{Mg(ClO}_4)_2$
- \times Robinson, McCoach and Lim [51], isopiestic vs CaBr_2

Col₂Recommended Values for the mean activity and osmotic coefficient of Col₂ in H₂O at 298.15 K

| <i>m/mol·kg⁻¹</i> | <i>γ</i> | <i>φ</i> | <i>a_w</i> | <i>ΔG^{ex}/J·kg⁻¹</i> |
|------------------------------|----------|----------|----------------------|--|
| .001 | .8872 | .9616 | .999948 | -1. |
| .002 | .8486 | .9482 | .999898 | -2. |
| .003 | .8216 | .9388 | .999848 | -3. |
| .004 | .8006 | .9315 | .999799 | -5. |
| .005 | .7832 | .9255 | .999750 | -6. |
| .006 | .7684 | .9204 | .999702 | -8. |
| .007 | .7554 | .9160 | .999654 | -10. |
| .008 | .7439 | .9121 | .999606 | -12. |
| .009 | .7335 | .9087 | .999558 | -15. |
| .010 | .7242 | .9056 | .999511 | -17. |
| .020 | .6608 | .8863 | .999042 | -45. |
| .030 | .6242 | .8774 | .998578 | -78. |
| .040 | .6598 | .8734 | .998114 | -114. |
| .050 | .6823 | .8722 | .997646 | -154. |
| .060 | .6691 | .8726 | .997174 | -195. |
| .070 | .5590 | .8743 | .996698 | -237. |
| .080 | .5512 | .8767 | .996217 | -281. |
| .090 | .5450 | .8797 | .995730 | -326. |
| .100 | .5401 | .8832 | .995238 | -371. |
| .200 | .5273 | .9272 | .990028 | -844. |
| .300 | .5410 | .9737 | .984337 | -1312. |
| .400 | .5652 | 1.0188 | .978215 | -1753. |
| .500 | .5962 | 1.0632 | .971679 | -2158. |
| .600 | .6330 | 1.1076 | .964721 | -2521. |
| .700 | .6756 | 1.1528 | .957323 | -2837. |
| .800 | .7247 | 1.1995 | .949458 | -3103. |
| .900 | .7810 | 1.2480 | .941101 | -3315. |
| 1.000 | .8453 | 1.2985 | .932227 | -3469. |
| 1.250 | 1.0497 | 1.4341 | .907660 | -3584. |
| 1.500 | 1.3353 | 1.5826 | .879588 | -3274. |
| 1.750 | 1.7334 | 1.7419 | .848102 | -2497. |
| 2.000 | 2.2872 | 1.9092 | .813530 | -1218. |
| 2.250 | 3.0536 | 2.0812 | .776401 | 587. |
| 2.500 | 4.1071 | 2.2547 | .737381 | 2937. |
| 2.750 | 5.5415 | 2.4266 | .697215 | 5842. |
| 3.000 | 7.4709 | 2.5940 | .656660 | 9304. |
| 3.250 | 10.0269 | 2.7543 | .616441 | 13317. |
| 3.500 | 13.3535 | 2.9052 | .577207 | 17871. |
| 3.750 | 17.5953 | 3.0448 | .539509 | 22948. |
| 4.000 | 22.8813 | 3.1714 | .503784 | 28526. |
| 4.250 | 29.3046 | 3.2837 | .470358 | 34578. |
| 4.500 | 36.8994 | 3.3808 | .439446 | 41075. |
| 4.750 | 45.6198 | 3.4620 | .411164 | 47983. |
| 5.000 | 55.3261 | 3.5269 | .385553 | 55269. |
| 5.250 | 65.7607 | 3.5755 | .362581 | 62694. |
| 5.500 | 76.6589 | 3.6079 | .342168 | 70823. |
| 5.750 | 87.5747 | 3.6246 | .324193 | 79017. |
| 6.000 | 98.1179 | 3.6265 | .308510 | 87441. |
| 6.250 | 107.8979 | 3.6145 | .294951 | 96059. |
| 6.500 ^(sat) | 116.5874 | 3.5899 | .283335 | 104837. |
| 6.750 | 123.9578 | 3.5541 | .273469 | 113742. |
| 7.000 | 129.9023 | 3.5088 | .265148 | 122750. |
| 7.250 | 134.4436 | 3.4560 | .258154 | 131832. |
| 7.500 | 137.7281 | 3.3979 | .252253 | 140968. |
| 7.750 | 140.0092 | 3.3367 | .247191 | 150142. |
| 8.000 | 141.6273 | 3.2750 | .242684 | 159341. |
| 8.250 | 142.9896 | 3.2154 | .238423 | 168559. |
| 8.500 | 144.5589 | 3.1611 | .234063 | 177795. |
| 8.750 | 146.8532 | 3.1148 | .229231 | 187056. |
| 9.000 | 150.4643 | 3.0801 | .222532 | 196353. |
| 9.250 | 156.0999 | 3.0602 | .216566 | 205707. |
| 9.500 | 164.6606 | 3.0587 | .207953 | 215143. |
| 9.750 | 177.3711 | 3.0793 | .197372 | 224698. |
| 10.000 | 196.0000 | 3.1260 | .184610 | 224414. |
| 10.100 | 205.6676 | 3.1529 | .178875 | 238357. |

| $m/mol \cdot kg^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln \gamma)$ | $\sigma(\gamma)$ |
|-----------------------|----------------|----------------------|------------------|
| .001 | .0002 | .0005 | .0004 |
| .010 | .0021 | .0044 | .0032 |
| .100 | .0129 | .0296 | .0160 |
| 1.000 | .0157 | .0696 | .0588 |
| 2.000 | .0166 | .0600 | .1373 |
| 5.000 | .0165 | .0661 | 3.6565 |
| 10.000 | .0343 | .0728 | 14.2765 |
| 10.100 | .0379 | .0763 | 15.6957 |

Coefficients of Correlating Equations

| | <u>Eqs 2</u> | | <u>Eqs 3</u> | |
|------|--------------------|-----------------------------------|--------------------|-----------------------------------|
| Par. | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> | <u>σ(coeff)</u> |
| 1 | .546554047801 | .521+00 | .9476445136+01 | .527+00 |
| 2 | -.5279072846+00 | .901+00 | -.1074768873+02 | .911+00 |
| 3 | .3531853068+01 | .602+00 | .7146954592+01 | .608+00 |
| 4 | -.1469357122+01 | .178+00 | -.2219520356+01 | .180+00 |
| 5 | .1860244467+00 | .194+01 | .2504491292+00 | .196-01 |

$$\sigma(\text{eqs 2}) = .404-01$$

$$\sigma(\text{eqs 3}) = .408-01$$

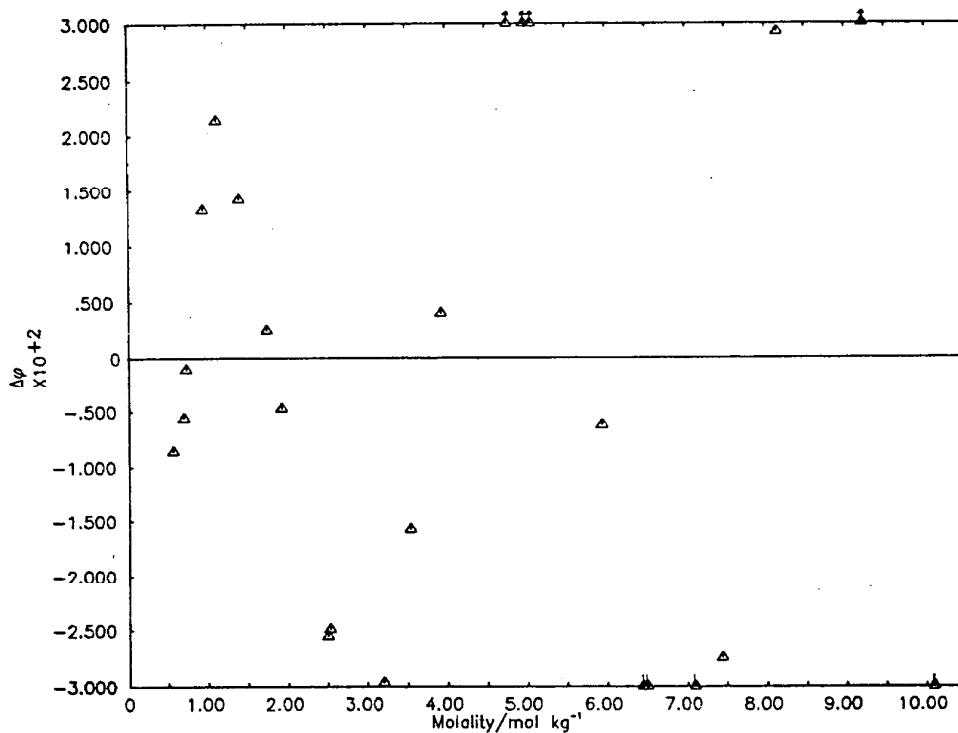
Experimental Data Employed in Generation of Correlating Equations

Robinson, McCoach; and Lim [5]. Isopiestic measurements, reference salt is $CaCl_2$. Assigned weight is 1.0.

| $m/mol \cdot kg^{-1}$ | \emptyset |
|-----------------------|-------------|
| •561000 | 1.0816 |
| •694500 | 1.1447 |
| •726000 | 1.1638 |
| •944500 | 1.2835 |
| 1.121000 | 1.3838 |
| 1.404000 | 1.5324 |
| 1.746000 | 1.7418 |
| 1.926000 | 1.8543 |
| 2.501000 | 2.2299 |
| 2.528000 | 2.2492 |
| 3.201000 | 2.6939 |
| 3.535000 | 2.9097 |
| 3.930000 | 3.1413 |
| 4.775000 | 3.5254 |
| 4.981000 | 3.5849 |
| 5.074000 | 3.5907 |
| 5.945000 | 3.6211 |
| 6.448000 | 3.5495 |
| 6.502000 | 3.5438 |
| 7.056000 | 3.4400 |
| 7.439000 | 3.3850 |
| 8.164000 | 3.2647 |
| 9.229000 | 3.1520 |
| 10.100000 | 3.1045 |

Comments

There is a fair amount of scatter in the isopiestic data of Robinson, McCoach, and Lim [51], probably attributable to slow decomposition of the salt in solution. A more precise set of measurements would be of value. Equations I could not be used to correlate the data and the table of recommended values and the deviation plot are based upon equations 3.

Deviation Plot For Col₂: $\Delta\phi$ vs molality

▲ Robinson, McCoach, and Lim [51], isopiestic vs CaCl_2

$\text{Co}(\text{NO}_3)_2$ Recommended Values for the mean activity and osmotic coefficient of $\text{Co}(\text{NO}_3)_2$ 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 | .8883 | .9622 | .999948 | -1. |
| .002 | .8504 | .9491 | .999897 | -2. |
| .003 | .8240 | .9400 | .999848 | -3. |
| .004 | .8034 | .9329 | .999798 | -5. |
| .005 | .7863 | .9270 | .999750 | -6. |
| .006 | .7716 | .9220 | .999701 | -8. |
| .007 | .7588 | .9176 | .999653 | -10. |
| .008 | .7474 | .9137 | .999605 | -12. |
| .009 | .7371 | .9102 | .999557 | -14. |
| .010 | .7277 | .9070 | .999510 | -17. |
| .020 | .6631 | .8556 | .999043 | -44. |
| .030 | .6241 | .8739 | .998584 | -77. |
| .040 | .5966 | .8663 | .998129 | -114. |
| .050 | .5758 | .8611 | .997676 | -154. |
| .060 | .5591 | .8575 | .997223 | -196. |
| .070 | .5455 | .8550 | .996771 | -240. |
| .080 | .5341 | .8532 | .996318 | -286. |
| .090 | .5243 | .8521 | .995864 | -333. |
| .100 | .5158 | .8515 | .995409 | -382. |
| .200 | .4690 | .8582 | .990766 | -915. |
| .300 | .4515 | .8747 | .985918 | -1494. |
| .400 | .4454 | .8946 | .980847 | -2092. |
| .500 | .4456 | .9162 | .975546 | -2694. |
| .600 | .4499 | .9389 | .970311 | -3292. |
| .700 | .4571 | .9625 | .964241 | -3880. |
| .800 | .4667 | .9868 | .958232 | -4455. |
| .900 | .4784 | 1.0116 | .951984 | -5013. |
| 1.000 | .4919 | 1.0370 | .945496 | -5551. |
| 1.250 | .5333 | 1.1024 | .928227 | -6797. |
| 1.500 | .5850 | 1.1704 | .909475 | -7882. |
| 1.750 | .6477 | 1.2407 | .889281 | -8785. |
| 2.000 | .7222 | 1.3127 | .867711 | -9492. |
| 2.250 | .8100 | 1.3864 | .844855 | -9991. |
| 2.500 | .9128 | 1.4613 | .820828 | -10273. |
| 2.750 | 1.0326 | 1.5371 | .795763 | -10328. |
| 3.000 | 1.1717 | 1.6135 | .765810 | -10152. |
| 3.250 | 1.3328 | 1.6902 | .743134 | -9738. |
| 3.500 | 1.5187 | 1.7668 | .715908 | -9082. |
| 3.750 | 1.7324 | 1.8429 | .688311 | -8183. |
| 4.000 | 1.9773 | 1.9184 | .660525 | -7039. |
| 4.250 | 2.2565 | 1.9927 | .632730 | -5648. |
| 4.500 | 2.5745 | 2.0656 | .605101 | -4012. |
| 4.750 | 2.9337 | 2.1366 | .577806 | -2133. |
| 5.000 | 3.3377 | 2.2056 | .551002 | -11. |
| 5.250 | 3.7893 | 2.2720 | .524834 | 2348. |
| 5.500 | 4.2907 | 2.3357 | .499432 | 4941. |
| 5.620(sat) | 4.5495 | 2.3651 | .487547 | 6267. |
| 5.750 | 4.8433 | 2.3961 | .474914 | 7762. |
| 5.790 | 4.9365 | 2.4054 | .471080 | 8234. |
| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln\gamma)$ | $\sigma(\gamma)$ | |
| .001 | .0001 | .0002 | .0002 | |
| .010 | .0008 | .0017 | .0013 | |
| .100 | .0026 | .0074 | .0038 | |
| 1.000 | .0016 | .0113 | .0055 | |
| 2.000 | .0016 | .0101 | .0073 | |
| 5.000 | .0035 | .0123 | .0412 | |
| 5.790 | .0054 | .0116 | .0574 | |

Coefficients of Correlating Equations

| <u>Eqs 1</u> | | <u>Eqs 2</u> | | <u>Eqs 3</u> | | |
|--------------|--------------------|-----------------------------------|--------------------|-----------------------------------|--------------------|---------|
| <u>Par</u> | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> | |
| 1 | .1548882687+01 | .429-01 | .9612031532+00 | .295+00 | .8409866200+01 | .307+00 |
| 2 | .3455882534+00 | .169-01 | .9095482822+01 | .922+00 | -.1019702100+02 | .962+00 |
| 3 | .5646717246-01 | .521-02 | -.5718314250+01 | .119+01 | .7838656857+01 | .124+01 |
| 4 | -.5060153065-02 | .526-03 | .2777416954+00 | .766+00 | -.3447124329+01 | .799+00 |
| 5 | | | -.7562225446+00 | .241+00 | .8078866323+00 | .252+00 |
| 6 | | | .8422392033-01 | .298-01 | -.7875830073 | .310-01 |

$$\begin{aligned}\sigma(\text{eqs 1}) &= .706-02 \\ \sigma(\text{eqs 2}) &= .717-02 \\ \sigma(\text{eqs 3}) &= .748-02\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Frolov, et al. [42]. Isopiestic measurements, reference salt is not given. Assigned weight is zero.

| <u>$m/mol \cdot kg^{-1}$</u> | <u>$\phi_{298.15}$</u> |
|---|-----------------------------------|
| 2.323000 | 1.4230 |
| 1.426000 | 1.2220 |
| 1.162000 | 1.0790 |
| .814000 | .9270 |
| 4.480000 | 2.0490 |
| 2.840000 | 1.5690 |
| 1.730300 | 1.2390 |
| 1.338200 | 1.1410 |

Jones and Getman [47]. Freezing point depression measurements. ϕ_L and ϕ_c data for $CoCl_2$ were used in treating these measurements. Assigned weight is zero.

| <u>$m/mol \cdot kg^{-1}$</u> | <u>$\phi_{298.15}$</u> |
|---|-----------------------------------|
| .074910 | .8305 |
| .150300 | .8041 |
| .302400 | .8159 |
| .456400 | .8554 |

Jones and Pearce [43]. Freezing point depression measurements. Assigned weight is zero.

| <u>$m/mol \cdot kg^{-1}$</u> | <u>$\phi_{298.15}$</u> |
|---|-----------------------------------|
| .010038 | .9833 |
| .025030 | .9526 |
| .050100 | .9095 |
| .075210 | .8967 |
| .100380 | .8818 |
| .252400 | .8945 |
| .510100 | .9422 |

Robinson and Brown [49]. Isopiestic measurements, reference salt is $CaCl_2$. Assigned weight is 1.0.

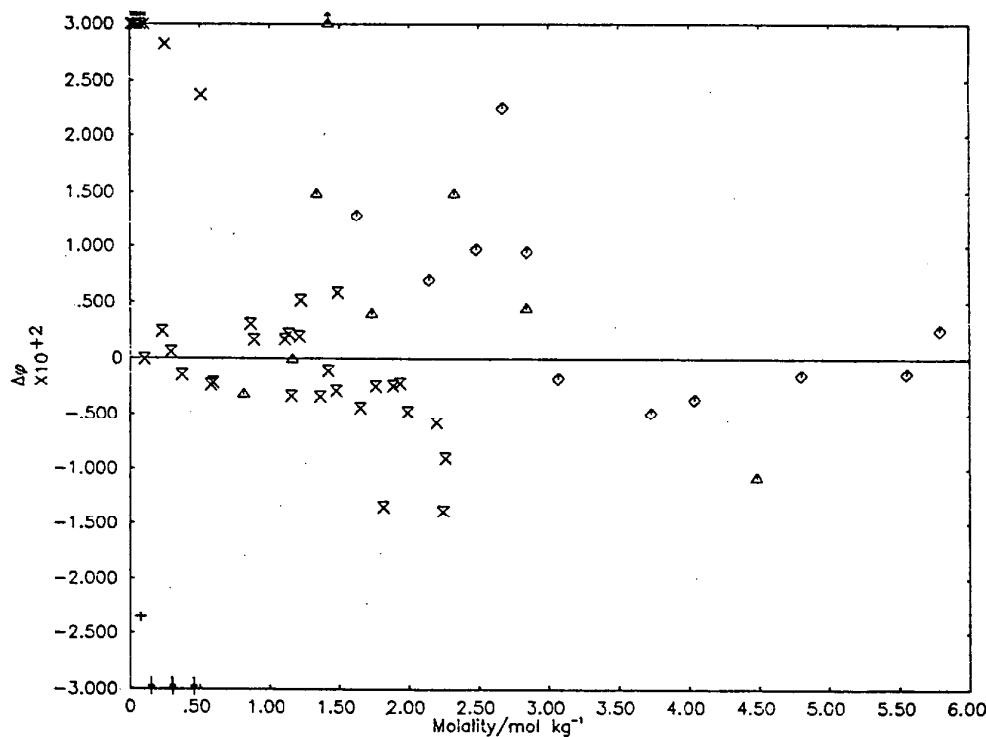
| <u>$m/mol \cdot kg^{-1}$</u> | <u>$\phi_{298.15}$</u> |
|---|-----------------------------------|
| 1.624000 | 1.2179 |
| 2.144000 | 1.3620 |
| 2.483000 | 1.4659 |
| 2.673000 | 1.5363 |
| 2.846000 | 1.5759 |
| 3.067000 | 1.6323 |
| 3.729000 | 1.8317 |
| 4.039000 | 1.9264 |
| 4.602000 | 2.1457 |
| 5.552000 | 2.3472 |
| 5.750000 | 2.4080 |

Robinson, Wilson, and Ayling [52]. Isopiestic measurements, reference salt is KCl . Assigned weight is 1.0.

| <u>$m/mol \cdot kg^{-1}$</u> | <u>$\phi_{298.15}$</u> |
|---|-----------------------------------|
| .102200 | .8513 |
| .229700 | .8650 |
| .293200 | .8740 |
| .371500 | .8872 |
| .579800 | .9319 |
| .596200 | .9359 |
| .864500 | 1.0058 |
| .888100 | 1.0103 |
| 1.109000 | 1.0669 |
| 1.137000 | 1.0747 |
| 1.155000 | 1.0739 |
| 1.214000 | 1.0948 |
| 1.223000 | 1.1004 |
| 1.362000 | 1.1292 |
| 1.421000 | 1.1476 |
| 1.477000 | 1.1612 |
| 1.487000 | 1.1727 |
| 1.656000 | 1.2079 |
| 1.760000 | 1.2410 |
| 1.815000 | 1.2458 |
| 1.886000 | 1.2772 |
| 1.935000 | 1.2916 |
| 1.590000 | 1.3050 |
| 2.198000 | 1.3651 |
| 2.244000 | 1.3708 |
| 2.261000 | 1.3806 |

Comments

The more recent isopiestic results of Frolov et al. [42], although less precise than the isopiestic results of Robinson et al. [49,52], are in fair agreement with them. The old freezing point depression measurements of Jones et al. [43,49] are given zero weight.



Deviation Plot For $\text{Co}(\text{NO}_3)_2$: $\Delta\theta$ vs molality

- ▲ Frolov et al. [42], isopiestic vs ?
- + Jones and Getman [49], freezing point depression
- ✗ Jones and Pearce [43], freezing point depression
- ◊ Robinson and Brown [51], isopiestic vs CaCl_2
- ☒ Robinson, Wilson and Ayling [52], isopiestic vs KCl

$[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ Recommended Values for the mean activity and osmotic coefficient of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ 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 | .9015 | .9688 | .999948 | -1. |
| .002 | .8715 | .9597 | .999896 | -1. |
| .003 | .8508 | .9532 | .999845 | -3. |
| .004 | .8344 | .9479 | .999795 | -4. |
| .005 | .8206 | .9433 | .999745 | -5. |
| .006 | .8084 | .9392 | .999695 | -7. |
| .007 | .7975 | .9353 | .999646 | -8. |
| .008 | .7876 | .9316 | .999597 | -10. |
| .009 | .7783 | .9280 | .999549 | -12. |
| .010 | .7697 | .9246 | .999500 | -14. |
| .020 | .7012 | .8935 | .999035 | -37. |
| .030 | .6487 | .8644 | .998599 | -66. |
| .040 | .6039 | .8358 | .998195 | -101. |
| .050 | .5641 | .8073 | .997821 | -141. |
| .060 | .5281 | .7789 | .997477 | -186. |
| .070 | .4951 | .7506 | .997165 | -236. |
| .080 | .4646 | .7221 | .996883 | -291. |
| .090 | .4363 | .6937 | .996631 | -350. |
| .100 | .4100 | .6652 | .996411 | -414. |
| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln\gamma)$ | $\sigma(\gamma)$ | |
| .001 | .0033 | .0074 | .0067 | |
| .010 | .0117 | .0322 | .0248 | |
| .100 | .0178 | .0743 | .0304 | |

Coefficients of Correlating Equations

| Par | Eqs 1 | | Eqs 2 | | Eqs 3 | |
|-----|----------------|------------------------|-----------------|------------------------|-----------------|------------------------|
| | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ |
| 1 | .8966847299+00 | .412-01 | -.8542577948+01 | .210+01 | .6377358634+01 | .674+00 |
| 2 | | | .5476724643+02 | .151+02 | -.5825971431+01 | .200+01 |
| 3 | | | -.7397029192+02 | .283+02 | | |

$$\sigma(\text{eqs 1}) = .873-02$$

$$\sigma(\text{eqs 2}) = .984-02$$

$$\sigma(\text{eqs 3}) = .884-02$$

Experimental Data Employed in Generation of Correlating Equations

Freezing point depression measurements of Harkins, Hall, and Roberts [56]. ϕ_L and ϕ_C data for CoCl_2 were used in the absence of any direct measurements. Assigned weight is 1.0.

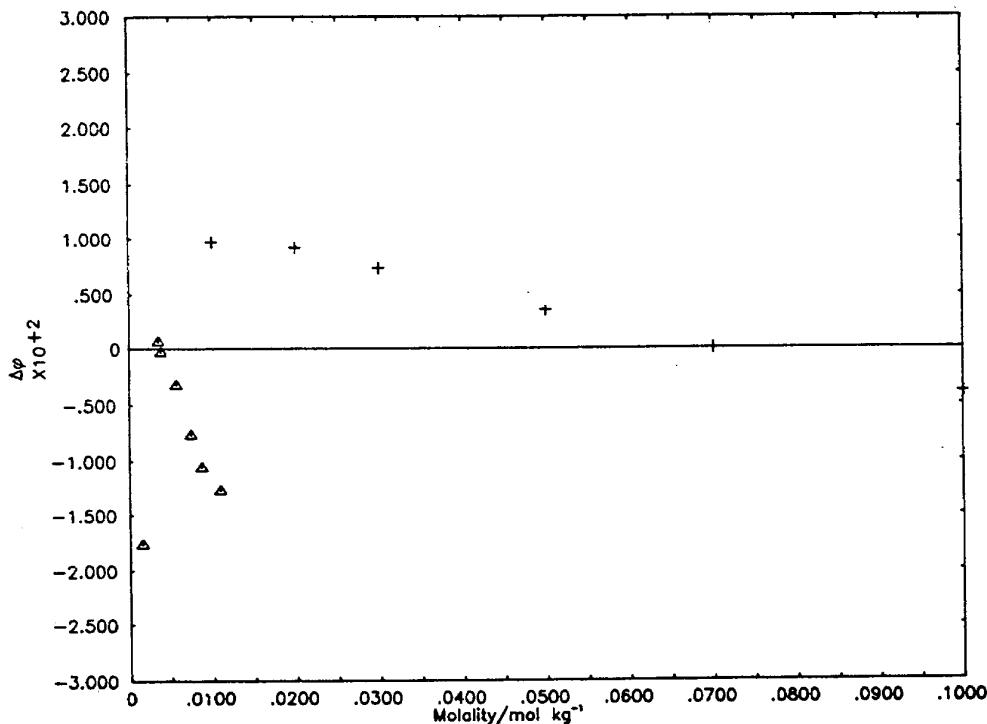
| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\phi_{298.15}$ |
|-----------------------------------|-----------------|
| .001540 | .9338 |
| .003540 | .9304 |
| .003860 | .9268 |
| .005110 | .9108 |
| .007450 | .8965 |
| .008710 | .8874 |
| .010920 | .8759 |

Vapor pressure osmometry data obtained at 37°C by Masterton and Scola [11]. ϕ_L and ϕ_c data for CoCl_2 were used to adjust the ϕ data to 25°C. Assigned weight is 1.0.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\phi_{298.15}$ |
|-------------------------------------|-----------------|
| .010000 | .9020 |
| .020000 | .8700 |
| .030000 | .8480 |
| .050000 | .8180 |
| .070000 | .7980 |
| .100000 | .7780 |

Comments

The old freezing point depression data of Harkins, Hall, and Roberts [10] appear to have been carefully performed. The agreement with the vapor pressure osmometry data [11] is fair.



Deviation Plot For $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$: $\Delta\phi$ vs molality

▲ Harkins, Hall and Roberts [10] - freezing point depression

+ Masterton and Scola [11] - vapor pressure osmometry

[Co (NH₃)₅ Cl] Cl₂

Recommended Values for the mean activity and osmotic coefficient of [Co(NH₃)₅Cl]Cl₂ in H₂O at 298.15 K

| <u>m/mol·kg⁻¹</u> | <u>γ</u> | <u>φ</u> | <u>a_w</u> | <u>ΔG^{ex}/J·kg⁻¹</u> |
|------------------------------|----------|----------|----------------------|--|
| .001 | .8897 | .9629 | .999948 | -1. |
| .002 | .8529 | .9505 | .999897 | -2. |
| .003 | .8274 | .9419 | .999847 | -3. |
| .004 | .8076 | .9353 | .999798 | -4. |
| .005 | .7912 | .9299 | .999749 | -6. |
| .006 | .7772 | .9253 | .999700 | -8. |
| .007 | .7651 | .9213 | .999652 | -10. |
| .008 | .7578 | .9190 | .999620 | -11. |

| <u>m/mol·kg⁻¹</u> | <u>σ(φ)</u> | <u>σ(λνγ)</u> | <u>σ(γ)</u> |
|------------------------------|-------------|---------------|-------------|
| .001 | .0010 | .0022 | .0019 |
| .008 | .0056 | .0124 | .0094 |

Coefficients of Correlating Equations

| <u>Par</u> | <u>Eqs 1</u> | | <u>Eqs 3</u> | |
|---|--------------------|-----------------|--------------------|-----------------|
| | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> | <u>σ(coeff)</u> |
| 1 | .1815736355+01 | .372+00 | .1004990834+02 | .169+01 |
| $\sigma(\text{eqs 1}) = .106 \cdot 10^{-3}$ | | | | |
| $\sigma(\text{eqs 3}) = .113 \cdot 10^{-3}$ | | | | |

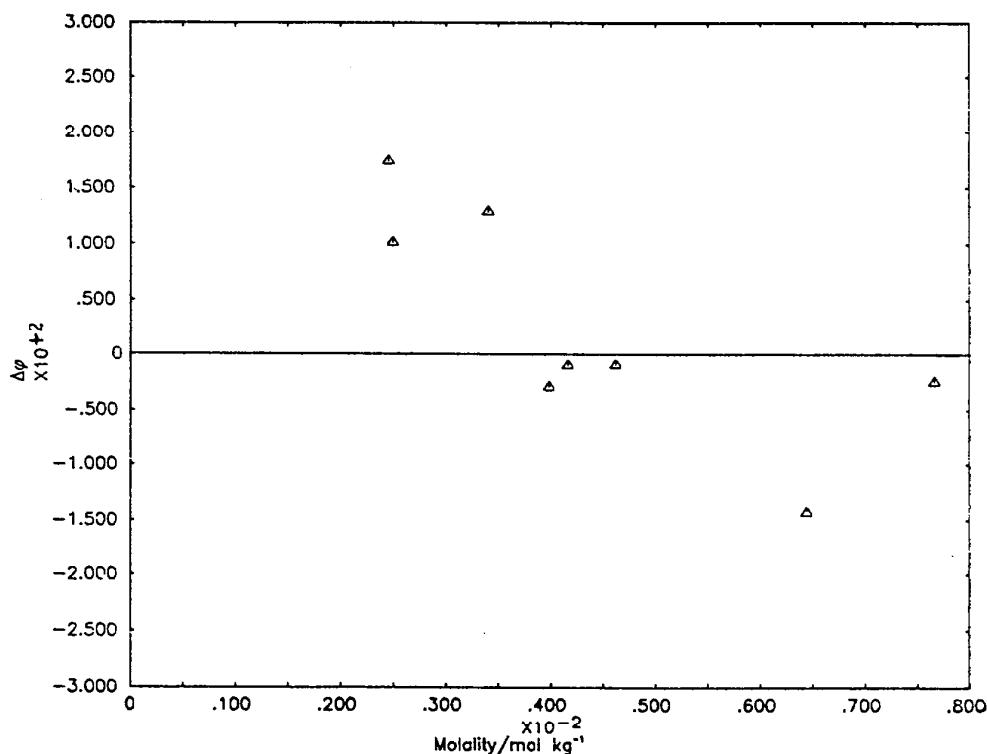
Experimental Data Employed in Generation of Correlating Equations

Harkins, Hall, and Roberts [10]. Freezing point depression measurements. φ_L and φ_v data for CoCl₂ were used in treating this data. A reasonable fit could not be obtained using eqs 2. Assigned weight is 1.0.

| <u>m/mol·kg⁻¹</u> | <u>φ_{298.15}</u> |
|------------------------------|---------------------------|
| .002450 | .9637 |
| .002490 | .9561 |
| .003400 | .9520 |
| .003980 | .9325 |
| .004160 | .9334 |
| .004620 | .9309 |
| .006440 | .9092 |
| .007660 | .9165 |

Comments

While a slightly better fit can be obtained for eqs 1 using 2 parameters, the values of the B coefficients so obtained is equal to 12.05 and seems physically unreasonable if one attempts to interpret that value in terms of an ionic size.



Deviation Plot for $[\text{Co}(\text{NH}_3)_5\text{Cl}_2]$: $\Delta\phi$ vs molality

▲ Markins, Hall and Roberts [10] - freezing point depression

[Co(NH₃)₅F]Cl₂

Recommended Values for the mean activity and osmotic coefficient of [Co(NH₃)₅F]Cl₂ in H₂O at 298.15 K

| <u>m/mol·kg⁻¹</u> | <u>γ</u> | <u>φ</u> | <u>a_w</u> | <u>ΔG^{ex}/J·kg⁻¹</u> |
|------------------------------|----------|----------|----------------------|--|
| .001 | .8853 | .9605 | .999948 | -1. |
| .002 | .8449 | .9460 | .999858 | -2. |
| .003 | .8162 | .9254 | .999848 | -3. |
| .004 | .7935 | .9270 | .999800 | -5. |
| .005 | .7744 | .9198 | .999751 | -7. |
| .006 | .7580 | .9135 | .999704 | -9. |
| .007 | .7435 | .9079 | .999657 | -11. |
| .008 | .7304 | .9029 | .999610 | -13. |
| .009 | .7186 | .8982 | .999563 | -15. |
| .010 | .7077 | .8940 | .999517 | -18. |
| .020 | .6308 | .8628 | .999068 | -48. |
| .030 | .5822 | .8424 | .998635 | -86. |
| .040 | .5467 | .8270 | .998214 | -128. |
| .050 | .5188 | .8147 | .997801 | -175. |
| .060 | .4960 | .8044 | .997395 | -226. |
| .070 | .4767 | .7955 | .996995 | -279. |
| .080 | .4600 | .7877 | .996600 | -336. |
| .090 | .4454 | .7808 | .996209 | -395. |
| .100 | .4324 | .7746 | .995823 | -456. |
| .200 | .3493 | .7321 | .992118 | -1166. |
| .300 | .3036 | .7058 | .988622 | -2003. |
| .400 | .2728 | .6861 | .985276 | -2931. |
| .500 | .2499 | .6702 | .982051 | -3931. |
| .600 | .2319 | .6569 | .978923 | -4990. |
| .700 | .2173 | .6456 | .975872 | -6102. |
| .800 | .2051 | .6359 | .972881 | -7259. |
| .900 | .1948 | .6276 | .969932 | -8457. |
| 1.000 | .1859 | .6207 | .967609 | -9691. |

| <u>m/mol·kg⁻¹</u> | <u>σ(φ)</u> | <u>σ(lnγ)</u> | <u>σ(γ)</u> |
|------------------------------|-------------|---------------|-------------|
| .001 | .0001 | .0001 | .0001 |
| .010 | .0004 | .0008 | .0006 |
| .100 | .0011 | .0033 | .0014 |
| 1.000 | .0023 | .0045 | .0008 |

Coefficients of Correlating Equations

| Par | Eqs 1 | | Eqs 2 | | Eqs 3 | |
|-----|-----------------|----------|-----------------|----------|-----------------|----------|
| | coefficient | σ(coeff) | coefficient | σ(coeff) | coefficient | σ(coeff) |
| 1 | .1104760370+01 | .223-01 | -.2714555741+01 | .196+00 | .6939240652+01 | .197+00 |
| 2 | -.3655036706+00 | .368-01 | -.1641391192+02 | .770+00 | -.1001455807+02 | .774+00 |
| 3 | .8167304991-01 | .221-01 | -.1239230111+02 | .103+01 | .8132463020+01 | .104+01 |
| 4 | | | -.7145381384+01 | .456+00 | -.2666591011+01 | .459+00 |

$$(\text{eqs 1}) = .235-02$$

$$(\text{eqs 2}) = .305-02$$

$$(\text{eqs 3}) = .306-02$$

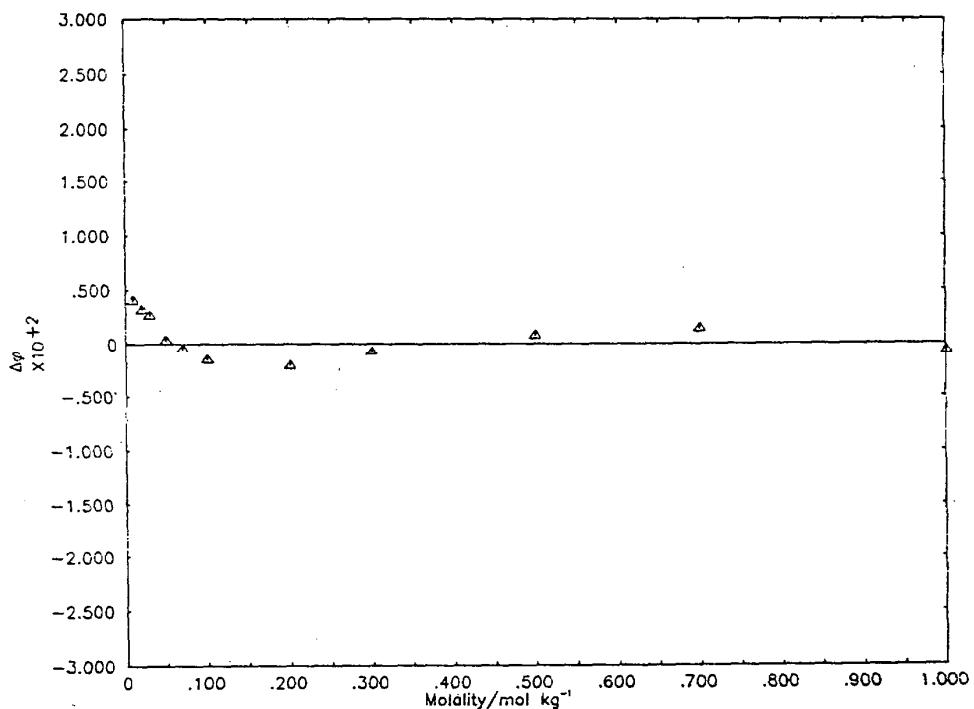
Experimental Data Employed in Generation of Correlating Equations

Masterton and Scola [11]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_c data for CoCl_2 were used in adjusting this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | ϕ |
|-------------------------------------|--------|
| •010000 | .8980 |
| •020000 | .8660 |
| •030000 | .8450 |
| •050360 | .8150 |
| •070660 | .7950 |
| •103060 | .7730 |
| •260000 | .7300 |
| •360000 | .7050 |
| •560000 | .6710 |
| •760000 | .6470 |
| 1.000000 | .6200 |

Comments

The above results are based solely upon vapor pressure osmometry measurements, as are the calculated results for the remaining cobalt compounds that follow.



Deviation Plot For $[\text{Co}(\text{NH}_3)_5\text{F}] \text{Cl}_2$: $\Delta\phi$ vs molality

▲ Masterton and Scola [11] - vapor pressure osmometry

[Co(NH₃)₅Cl](ClO₄)₂Recommended Values for the mean activity and osmotic coefficient of [Co(NH₃)₅Cl](ClO₄)₂ in H₂O at 298.15 K

| <i>m/mol·kg⁻¹</i> | <i>γ</i> | <i>φ</i> | <i>a_w</i> | <i>ΔG^{ex/J·kg⁻¹}</i> |
|------------------------------|----------|----------|----------------------|--|
| .001 | .8876 | .9617 | .999948 | -1. |
| .002 | .8487 | .9480 | .999898 | -2. |
| .003 | .8213 | .9382 | .999848 | -3. |
| .004 | .7956 | .9203 | .999799 | -5. |
| .005 | .7814 | .9236 | .999750 | -6. |
| .006 | .7657 | .9177 | .999702 | -8. |
| .007 | .7517 | .9124 | .999655 | -10. |
| .008 | .7392 | .9076 | .999608 | -12. |
| .009 | .7278 | .9032 | .999561 | -15. |
| .010 | .7173 | .8991 | .999514 | -17. |
| .020 | .6418 | .8682 | .999062 | -46. |
| .030 | .5929 | .8466 | .998628 | -82. |
| .040 | .5566 | .8299 | .998207 | -124. |
| .050 | .5278 | .8164 | .997796 | -169. |
| .060 | .5043 | .8053 | .997392 | -219. |
| .070 | .4846 | .7962 | .996992 | -271. |
| .080 | .4680 | .7889 | .996595 | -326. |
| .090 | .4538 | .7833 | .996197 | -384. |
| .100 | .4416 | .7793 | .995797 | -444. |
| <i>m/mol·kg⁻¹</i> | | | | |
| <i>σ(φ)</i> | | | | |
| .001 | .0001 | .0003 | .0003 | |
| .010 | .0005 | .0015 | .0011 | |
| .100 | .0000 | .0019 | .0008 | |

Coefficients of Correlating Equations

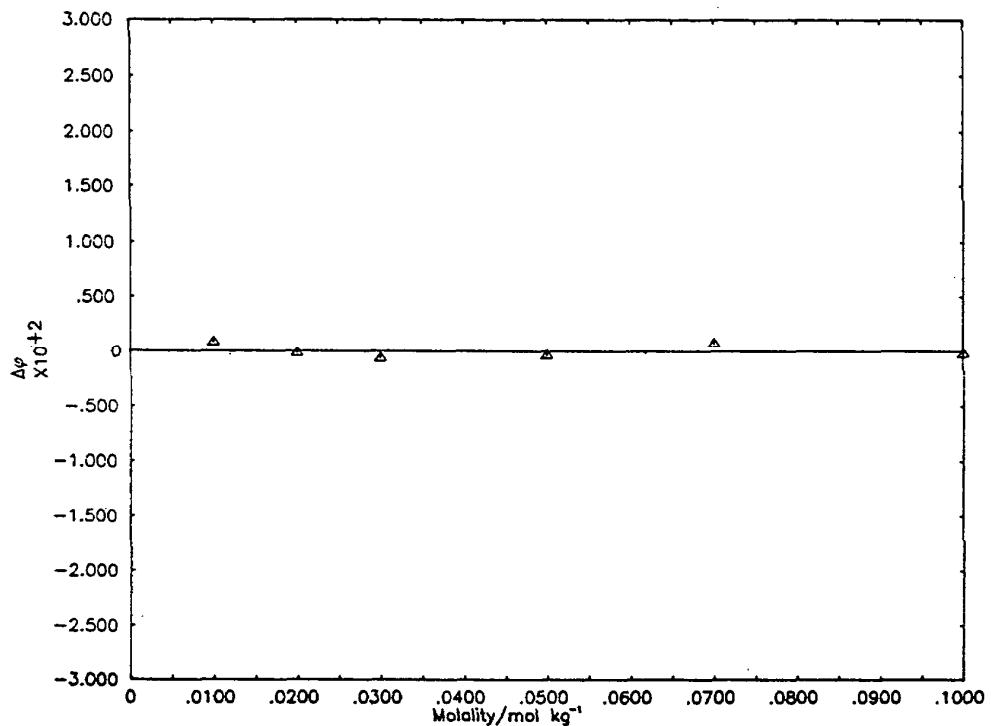
| Par | <u>Eqs 1</u> | | <u>Eqs 2</u> | | <u>Eqs 3</u> | |
|-----|--------------------|-----------------|--------------------|-----------------|--------------------|-----------------|
| | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> | <u>σ(coeff)</u> |
| 1 | .19434839640+01 | .100+00 | | | | |
| 2 | -.28338359161+01 | .267+00 | -.2344230953+01 | .106+00 | .6876510176+01 | .381+00 |
| 3 | .90269417562+01 | .118+01 | .1207929462+02 | .313+00 | -.7271154253+01 | .112+01 |

$$\begin{aligned}\sigma(\text{eqs 1}) &= .840-03 \\ \sigma(\text{eqs 2}) &= .124-02 \\ \sigma(\text{eqs 3}) &= .144-02\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Masterton and Scola [11]. Vapor pressure osmometry measurements performed at 37°C. φ_L and φ_c data for CoCl₂ were used in adjusting this data to 25°C. Assigned weight is 1.0.

| <i>m/mol·kg⁻¹</i> | <i>φ_{298.15}</i> |
|------------------------------|---------------------------|
| .010000 | .9000 |
| .020000 | .8680 |
| .030000 | .8460 |
| .050000 | .8160 |
| .070000 | .7970 |
| .100000 | .7790 |



Deviation Plot For $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{ClO}_4)_2$: $\Delta\theta$ vs molality

▲ Masterton and Scola [11] - vapor pressure osmometry

$$[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{CH}_2\text{COO}](\text{NO}_3)_2$$

Recommended Values for the mean activity and osmotic coefficient of $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{CH}_2\text{COO}](\text{NO}_3)_2$ 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 | .8445 | .5601 | .999948 | -1. |
| .002 | .8435 | .9452 | .999998 | -2. |
| .003 | .8142 | .9343 | .999849 | -3. |
| .004 | .7910 | .9255 | .999800 | -5. |
| .005 | .7715 | .9180 | .999752 | -7. |
| .006 | .7546 | .9114 | .999704 | -9. |
| .007 | .7397 | .9055 | .999657 | -11. |
| .008 | .7263 | .9002 | .999611 | -13. |
| .009 | .7141 | .8953 | .999565 | -16. |
| .010 | .7029 | .8908 | .999519 | -18. |
| .020 | .6232 | .8574 | .999074 | -49. |
| .030 | .5727 | .8352 | .998647 | -88. |
| .040 | .5358 | .8183 | .998233 | -132. |
| .050 | .5067 | .8046 | .997828 | -180. |
| .060 | .4829 | .7931 | .997432 | -233. |
| .070 | .4627 | .7831 | .997042 | -288. |
| .080 | .4453 | .7744 | .996658 | -347. |
| .090 | .4301 | .7665 | .996279 | -408. |
| .100 | .4165 | .7594 | .995904 | -472. |
| .200 | .3257 | .7094 | .992361 | -1218. |
| .300 | .2814 | .6757 | .989104 | -2105. |
| .400 | .2482 | .6473 | .986104 | -3096. |

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln\gamma)$ | $\sigma(\gamma)$ |
|-----------------------------------|----------------|---------------------|------------------|
| .001 | .0001 | .0001 | .0001 |
| .010 | .0004 | .0008 | .0006 |
| .100 | .0007 | .0023 | .0010 |
| .400 | .0014 | .0026 | .0007 |

Coefficients of Correlating Equations

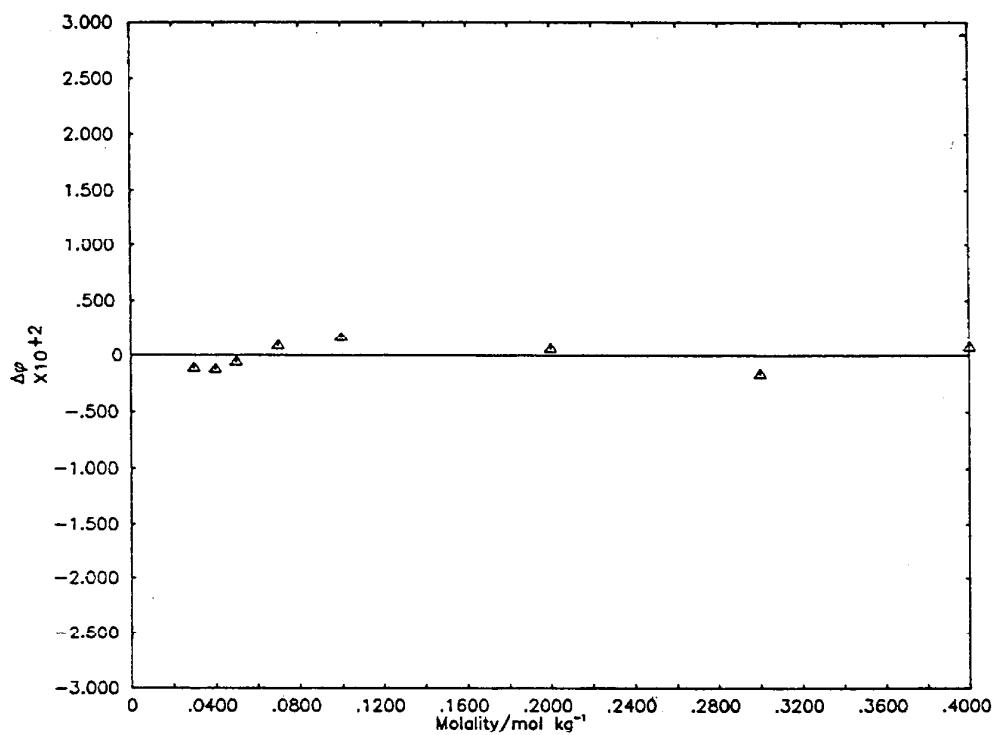
| <u>Eqs 1</u> | | <u>Eqs 2</u> | | <u>Eqs 3</u> | | |
|--------------|--------------------|--------------------|--------------------|--------------------|--------------------|---------|
| <u>Par</u> | <u>coefficient</u> | <u>coefficient</u> | <u>coefficient</u> | <u>coefficient</u> | <u>coefficient</u> | |
| 1 | .9541461770+00 | .336-01 | -.5645279676+01 | .324+00 | .5895451600+01 | .398-01 |
| 2 | -.2842869067+00 | .970-01 | .3156055849+02 | .200+01 | -.6633590679+01 | .142+00 |
| 3 | -.1232895187+00 | .114+00 | -.4124941550+02 | .417+01 | .3136811707+01 | .133+00 |
| 4 | | | .2245898278+02 | .285+01 | | |

$$\begin{aligned}\sigma(\text{eqs 1}) &= .145-02 \\ \sigma(\text{eqs 2}) &= .157-02 \\ \sigma(\text{eqs 3}) &= .641-03\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Berka and Masterton [12]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_C data for CoCl_2 were used in adjusting this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\phi_{298.15}$ |
|-----------------------------------|-----------------|
| .030000 | .8340 |
| .040000 | .8170 |
| .050000 | .8040 |
| .070000 | .7840 |
| .100000 | .7610 |
| .200000 | .7100 |
| .300000 | .6740 |
| .400000 | .6480 |



Deviation Plot For $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{CH}_2\text{COO}](\text{NO}_3)_2$: $\Delta\phi$ vs molality

▲ Berka and Masterton [12] - vapor pressure osmometry

[Co(NH₃)₅CH₃CH₂COO]I₂Recommended Values for the mean activity and osmotic coefficient of [Co(NH₃)₅CH₃CH₂COO]I₂ in H₂O at 298.15 K

| <i>m/mol·kg⁻¹</i> | <i>γ</i> | <i>φ</i> | <i>a_w</i> | <i>ΔG^{ex/J·kg⁻¹}</i> |
|------------------------------|----------|----------|----------------------|--|
| .001 | .8843 | .9600 | .999948 | -1. |
| .002 | .8431 | .9450 | .999898 | -2. |
| .003 | .8130 | .9340 | .999849 | -3. |
| .004 | .7905 | .9252 | .999800 | -5. |
| .005 | .7709 | .9177 | .999752 | -7. |
| .006 | .7540 | .9111 | .999705 | -9. |
| .007 | .7390 | .9052 | .999658 | -11. |
| .008 | .7255 | .8998 | .999611 | -13. |
| .009 | .7133 | .8949 | .999565 | -16. |
| .010 | .7021 | .8904 | .999519 | -18. |
| .020 | .6225 | .8572 | .999074 | -49. |
| .030 | .5723 | .8354 | .998646 | -88. |
| .040 | .5352 | .8192 | .998231 | -132. |
| .050 | .5073 | .8063 | .997824 | -180. |
| .060 | .4840 | .7956 | .997423 | -233. |
| .070 | .4644 | .7865 | .997029 | -288. |
| .080 | .4476 | .7787 | .996639 | -347. |
| .090 | .4329 | .7718 | .996253 | -408. |
| .100 | .4199 | .7656 | .995871 | -471. |
| .200 | .3381 | .7254 | .992190 | -1204. |
| .300 | .2932 | .6992 | .988727 | -2066. |
| .400 | .2616 | .6752 | .985510 | -3022. |
| .500 | .2365 | .6493 | .982696 | -4057. |

| <i>m/mol·kg⁻¹</i> | <i>σ(φ)</i> | <i>σ(lnγ)</i> | <i>σ(γ)</i> |
|------------------------------|-------------|---------------|-------------|
| .001 | .0000 | .0001 | .0001 |
| .010 | .0002 | .0005 | .0004 |
| .100 | .0005 | .0017 | .0007 |
| .500 | .0011 | .0020 | .0005 |

Coefficients of Correlating Equations

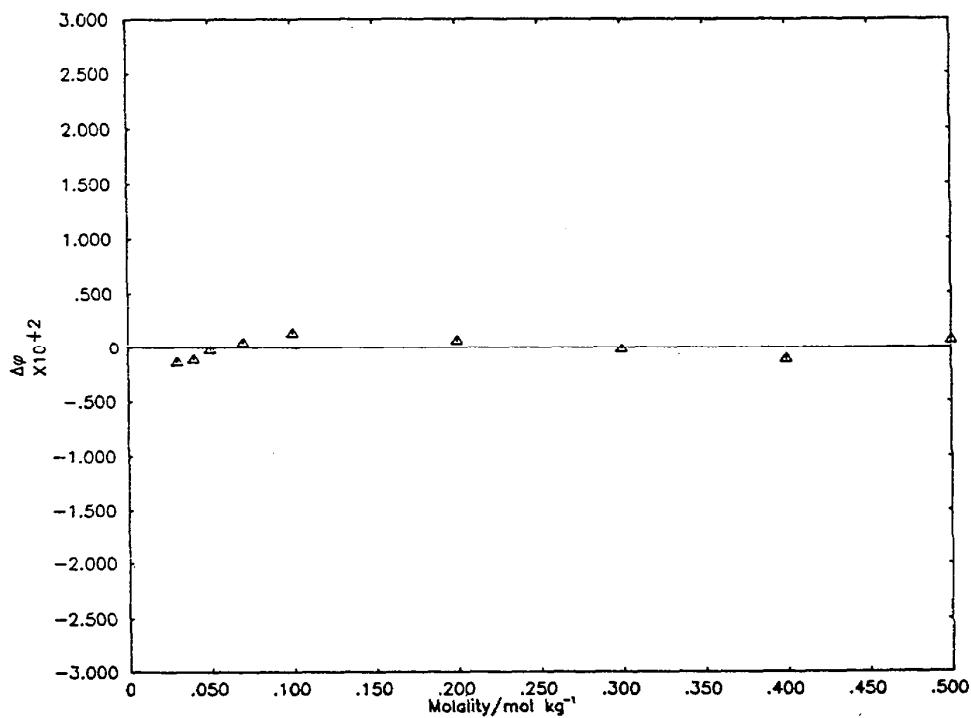
| | <u>Eqs 1</u> | | <u>Eqs 2</u> | | <u>Eqs 3</u> | |
|-----|--------------------|-----------------|--------------------|-----------------|--------------------|-----------------|
| Par | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> | <u>σ(coeff)</u> |
| 1 | .8466768420+00 | .199-01 | -.5099271970+01 | .341+00 | .4993484018+01 | .930-01 |
| 2 | .1713789975+00 | .569-01 | .2785496047+02 | .190+01 | -.3036828505+01 | .122+00 |
| 3 | -.4523432182+00 | .532-01 | -.3152714522+02 | .357+01 | | |
| 4 | | | .1471324779+02 | .220+01 | | |

$$\begin{aligned}\sigma(\text{eqs 1}) &= .114-02 \\ \sigma(\text{eqs 2}) &= .242-02 \\ \sigma(\text{eqs 3}) &= .566-02\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Berka and Masterton [12]. Vapor pressure osmometry measurements performed at 37°C. φ_L and φ_c data for CoCl₂ were used to adjust this data to 25°C. Assigned weight is 1.0.

| <i>m/mol·kg⁻¹</i> | <i>φ_{298.15}</i> |
|------------------------------|---------------------------|
| .030000 | .8340 |
| .040000 | .8180 |
| .050000 | .8060 |
| .070000 | .7870 |
| .100000 | .7670 |
| .200000 | .7260 |
| .300000 | .6990 |
| .400000 | .6740 |
| .500000 | .6500 |



Deviation Plot For $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}]_{\text{I}}_2$: $\Delta\phi$ vs molality

▲ Berka and Masterton [12] - vapor pressure osmometry

$$[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{CH}_2\text{COO}]\text{Br}_2$$

Recommended Values for the mean activity and osmotic coefficient of $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{CH}_2\text{COO}]\text{Br}_2$ 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 | .8848 | .9603 | .999948 | -1. |
| .002 | .8441 | .9455 | .999898 | -2. |
| .003 | .8151 | .9348 | .999848 | -3. |
| .004 | .7921 | .9262 | .999800 | -5. |
| .005 | .7728 | .9188 | .999752 | -7. |
| .006 | .7562 | .9124 | .999704 | -9. |
| .007 | .7414 | .9067 | .999657 | -11. |
| .008 | .7282 | .9015 | .999610 | -13. |
| .009 | .7162 | .8967 | .999564 | -15. |
| .010 | .7051 | .8923 | .999518 | -18. |
| .020 | .6268 | .8601 | .999071 | -49. |
| .030 | .5773 | .8388 | .998641 | -87. |
| .040 | .5412 | .8228 | .998223 | -130. |
| .050 | .5129 | .8100 | .997813 | -178. |
| .060 | .4897 | .7993 | .997411 | -229. |
| .070 | .4701 | .7902 | .997015 | -284. |
| .080 | .4532 | .7821 | .996624 | -341. |
| .090 | .4384 | .7750 | .996237 | -401. |
| .100 | .4253 | .7687 | .995854 | -464. |
| .200 | .3423 | .7265 | .992170 | -1168. |
| .300 | .2974 | .7020 | .988683 | -2040. |
| .400 | .2677 | .6848 | .985305 | -2983. |
| .500 | .2459 | .6718 | .982011 | -3996. |
| .600 | .2290 | .6615 | .978779 | -5066. |
| .700 | .2155 | .6532 | .975590 | -6185. |
| .800 | .2043 | .6466 | .972428 | -7347. |
| .900 | .1949 | .6415 | .969278 | -8546. |
| 1.000 | .1869 | .6377 | .966124 | -9778. |
| 1.200 | .1741 | .6334 | .959750 | -12327. |

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln y)$ | $\sigma(\gamma)$ |
|-----------------------------------|----------------|-----------------|------------------|
| .001 | .0001 | .0002 | .0001 |
| .010 | .0006 | .0012 | .0009 |
| .100 | .0019 | .0054 | .0023 |
| 1.000 | .0023 | .0063 | .0012 |
| 1.200 | .0038 | .0076 | .0013 |

Coefficients of Correlating Equations

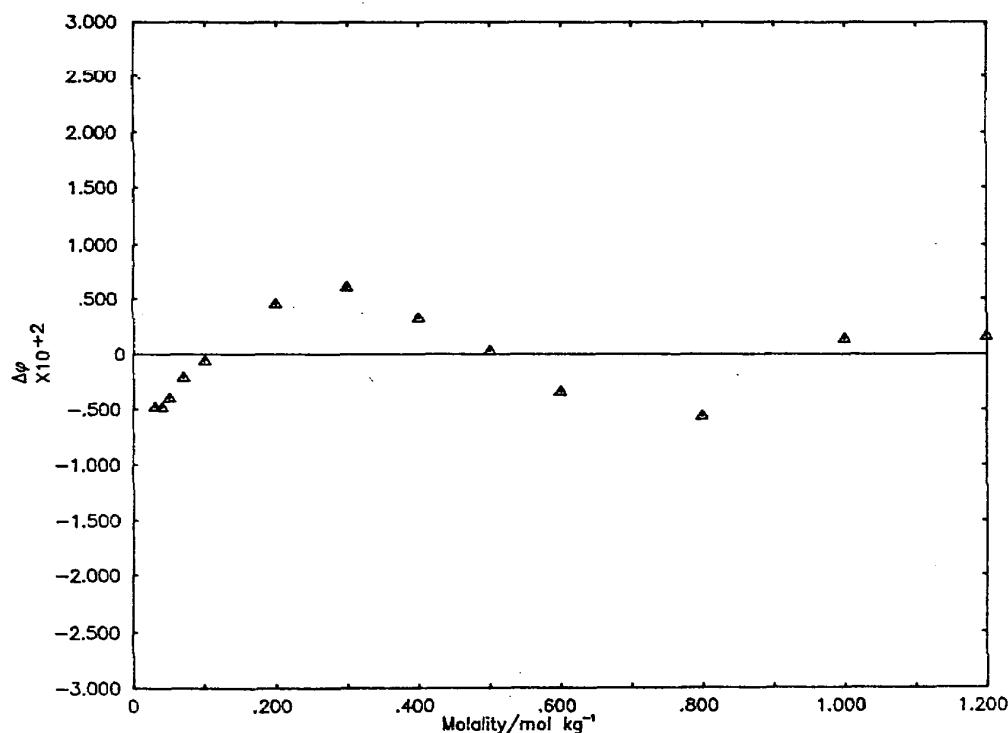
| Par | <u>Eqs 1</u> | | <u>Eqs 2</u> | | <u>Eqs 3</u> | |
|-----|-----------------|------------------------|-----------------|------------------------|-----------------|------------------------|
| | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ |
| 1 | .1012607877+01 | .338-01 | -.5267259149+01 | .214+00 | .5907520192+01 | .103+00 |
| 2 | -.2689611250+00 | .513-01 | .2989601315+02 | .115+01 | -.6305848230+01 | .353+00 |
| 3 | .7139830888-01 | .243-01 | -.3971298376+02 | .233+01 | .3515590473+01 | .424+00 |
| 4 | | | .2851164026+02 | .206+01 | -.7291162271+00 | .170+00 |
| 5 | | | -.7978924105+01 | .666+00 | | |

$\sigma(\text{eqs 1}) = .428-02$
 $\sigma(\text{eqs 2}) = .204-02$
 $\sigma(\text{eqs 3}) = .219-02$

Experimental Data Employed in Generation of Correlating Equations

Berka and Masterton [12]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_C data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\phi_{298.15}$ |
|-------------------------------------|-----------------|
| .030000 | .8340 |
| .040000 | .8180 |
| .050000 | .8060 |
| .070000 | .7880 |
| .100000 | .7660 |
| .200000 | .7310 |
| .300000 | .7080 |
| .400000 | .6880 |
| .500000 | .6720 |
| .600000 | .6580 |
| .800000 | .6410 |
| 1.000000 | .6390 |
| 1.200000 | .6350 |

Deviation Plot For $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{CH}_2\text{COO}]\text{Br}_2$: $\Delta\phi$ vs molality

▲ Berka and Masterton [12] - vapor pressure osmometry

$[Co(NH_3)_5CH_3CH_2COO]Cl_2$ Recommended Values for the mean activity and osmotic coefficient of $[Co(NH_3)_5CH_3CH_2COO]Cl_2$ in H_2O at 298.15 K

| $m/mol \cdot kg^{-1}$ | γ | ϕ | a_w | $\Delta G^{ex} / J \cdot kg^{-1}$ |
|-----------------------|----------------|----------------------|------------------|-----------------------------------|
| .001 | .8244 | .9600 | .999948 | -1. |
| .002 | .8433 | .9451 | .999898 | -2. |
| .003 | .8141 | .9342 | .999849 | -3. |
| .004 | .7908 | .9254 | .999800 | -5. |
| .005 | .7713 | .9179 | .999752 | -7. |
| .006 | .7544 | .9113 | .999705 | -9. |
| .007 | .7395 | .9055 | .999657 | -11. |
| .008 | .7261 | .9002 | .999611 | -13. |
| .009 | .7139 | .8953 | .999565 | -16. |
| .010 | .7028 | .8908 | .999519 | -18. |
| .020 | .6234 | .8578 | .999073 | -49. |
| .030 | .5734 | .8261 | .998645 | -88. |
| .040 | .5370 | .8200 | .998229 | -131. |
| .050 | .5025 | .8072 | .997821 | -180. |
| .060 | .4853 | .7966 | .997420 | -232. |
| .070 | .4658 | .7876 | .997025 | -287. |
| .080 | .4491 | .7799 | .996633 | -345. |
| .090 | .4345 | .7732 | .996246 | -406. |
| .100 | .4216 | .7673 | .995862 | -469. |
| .200 | .3417 | .7313 | .992126 | -1198. |
| .300 | .3003 | .7145 | .988482 | -2047. |
| .400 | .2737 | .7053 | .984867 | -2978. |
| .500 | .2548 | .7001 | .981260 | -3969. |
| .600 | .2404 | .6971 | .977648 | -5009. |
| .700 | .2291 | .6956 | .974026 | -6087. |
| .800 | .2198 | .6951 | .970393 | -7199. |
| .900 | .2121 | .6953 | .966747 | -8339. |
| 1.000 | .2056 | .6959 | .963088 | -9604. |
| 1.250 | .1927 | .6989 | .953881 | -12508. |
| 1.500 | .1832 | .7030 | .944598 | -15618. |
| 1.750 | .1759 | .7078 | .935249 | -18812. |
| 2.000 | .1701 | .7128 | .925845 | -22075. |
| 2.250 | .1653 | .7180 | .916394 | -25396. |
| 2.400 | .1629 | .7211 | .910706 | -27412. |
| $m/mol \cdot kg^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln \gamma)$ | $\sigma(\gamma)$ | |
| .001 | .0000 | .0001 | .0001 | |
| .010 | .0003 | .0006 | .0005 | |
| .100 | .0015 | .0036 | .0015 | |
| 1.000 | .0022 | .0087 | .0018 | |
| 2.000 | .0038 | .0089 | .0015 | |
| 2.400 | .0050 | .0093 | .0015 | |

Coefficients of Correlating Equations

| | Eqs 1 | | | Eqs 2 | | | |
|-----|----------------|------------------------|--|-----------------|------------------------|-----------------|------------------------|
| Par | coefficients | $\sigma(\text{coeff})$ | | coefficients | $\sigma(\text{coeff})$ | coefficients | $\sigma(\text{coeff})$ |
| 1 | .8921256715+00 | .135-01 | | -.8819392558+01 | .108+01 | .5707831492+01 | .143+00 |
| 2 | .1886247581-01 | .753-02 | | -.5699791392+02 | .771+01 | -.5526550862+01 | .348+00 |
| 3 | | | | -.1220204006+03 | .224+02 | .2910569975+01 | .294+00 |
| 4 | | | | -.1561070231+03 | .334+02 | -.6069771021+00 | .832-01 |
| 5 | | | | -.1131260227+03 | .269+02 | | |
| 6 | | | | -.4312119692+02 | .112+02 | | |
| 7 | | | | -.6719160104+01 | .187+01 | | |

$\sigma(\text{eqs 1}) = .775-02$

$\sigma(\text{eqs 2}) = .732-02$

$\sigma(\text{eqs 3}) = .711-02$

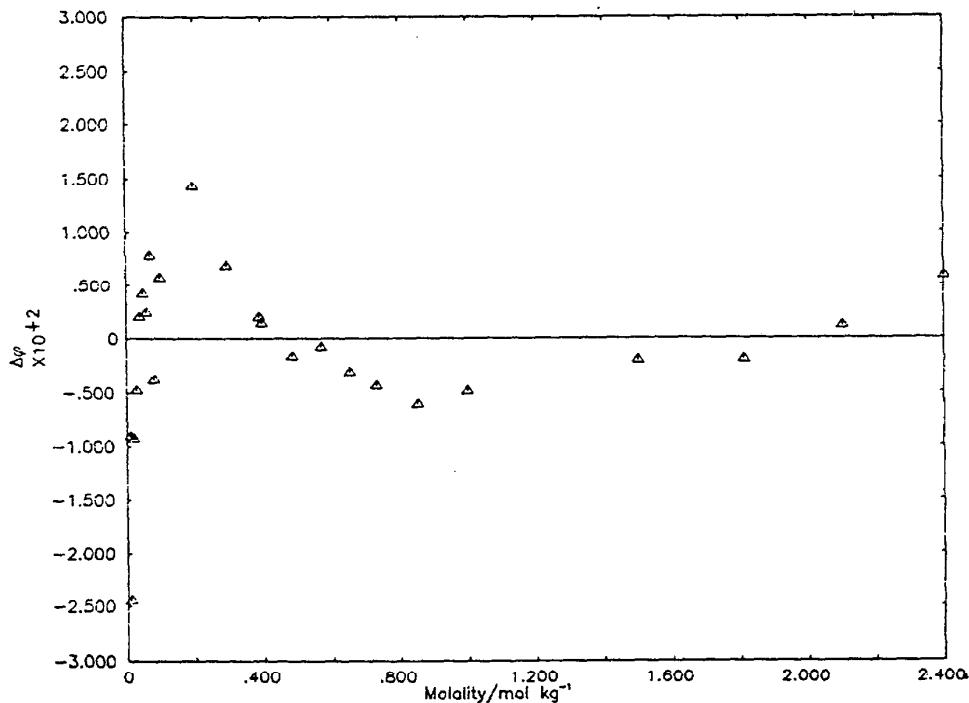
Experimental Data Employed in Generation of Correlating Equations

Berka and Masterton [12]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_C data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\phi_{298.15}$ |
|-------------------------------------|-----------------|
| .010300 | .8650 |
| .010400 | .8800 |
| .020200 | .8480 |
| .030200 | .8310 |
| .040000 | .8220 |
| .050300 | .8110 |
| .060000 | .7990 |
| .070600 | .7950 |
| .081200 | .7760 |
| .100000 | .7730 |
| .198000 | .7460 |
| .295000 | .7220 |
| .390000 | .7080 |
| .396000 | .7070 |
| .485000 | .6990 |
| .570000 | .6970 |
| .653000 | .6930 |
| .732000 | .6910 |
| .852000 | .6890 |
| .999000 | .6910 |
| 1.500000 | .7010 |
| 1.810000 | .7070 |
| 2.100000 | .7160 |
| 2.400000 | .7270 |

Comments

The fit using equations 2 is difficult for this system.



Deviation Plot For $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{CH}_2\text{COO}] \text{Cl}_2$: $\Delta\phi$ vs molality

▲ Berka and Masterton [12] - vapor pressure osmometry

$$[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}](\text{NO}_3)_2$$

Recommended Values for the mean activity and osmotic coefficient of $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}](\text{NO}_3)_2$ 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 | .8837 | .9596 | .999948 | -1. |
| .002 | .8420 | .9444 | .999898 | -2. |
| .003 | .8123 | .9332 | .999849 | -3. |
| .004 | .7887 | .9242 | .999800 | -5. |
| .005 | .7689 | .9165 | .999752 | -7. |
| .006 | .7517 | .9097 | .999705 | -9. |
| .007 | .7365 | .9037 | .999658 | -11. |
| .008 | .7229 | .8982 | .999612 | -13. |
| .009 | .7105 | .8932 | .999566 | -16. |
| .010 | .6951 | .8886 | .999520 | -18. |
| .020 | .6188 | .8551 | .999076 | -50. |
| .030 | .5685 | .8335 | .998649 | -89. |
| .040 | .5323 | .8178 | .998234 | -133. |
| .050 | .5043 | .8057 | .997825 | -182. |

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln\gamma)$ | $\sigma(\gamma)$ |
|-----------------------------------|----------------|---------------------|------------------|
| .001 | .0001 | .0003 | .0002 |
| .010 | .0008 | .0019 | .0013 |
| .100 | .0083 | .0090 | .0038 |

Coefficients of Correlating Equations

| Par | Eqs 2 | | Eqs 3 | |
|-----|-----------------|------------------------|-----------------|------------------------|
| | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ |
| 1 | -.4765183294+01 | .915-01 | -.5300274697+01 | .312+00 |
| 2 | .1969020635+02 | .367+00 | -.3449700277+01 | .125+01 |

$$\begin{aligned}\sigma(\text{eqs 2}) &= .295-03 \\ \sigma(\text{eqs 3}) &= .101-02\end{aligned}$$

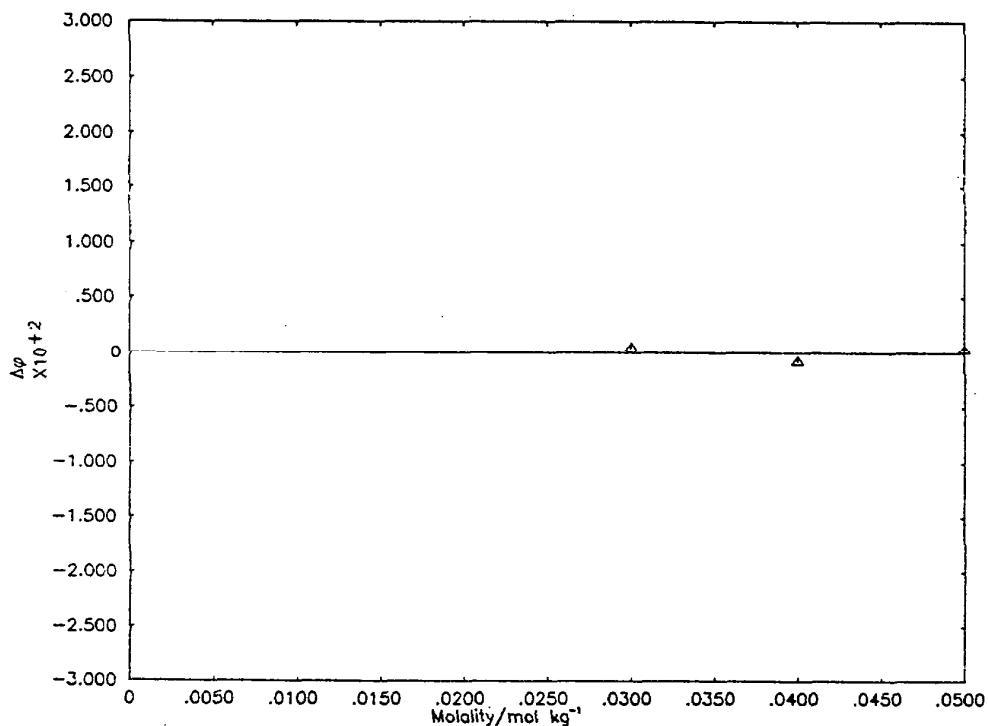
Experimental Data Employed in Generation of Correlating Equations

Berka and Masterton [12]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_c data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\phi_{298.15}$ |
|-----------------------------------|-----------------|
| .030000 | .8340 |
| .040000 | .8170 |
| .050000 | .8060 |

Comments

It was not possible to obtain a fit for this system using eqs 1. The table of recommended values and the deviation plot are based on eqs 3.



Deviation Plot For $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}](\text{NO}_3)_2$: $\Delta\theta$ vs molality

▲ Berka and Masterton [12] - vapor pressure osmometry

$[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}]I_2$

Recommended Values for the mean activity and osmotic coefficient of $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}]I_2$ 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 | .8846 | .9601 | .999948 | -1. |
| .002 | .8437 | .9453 | .999898 | -2. |
| .003 | .8145 | .9345 | .999849 | -3. |
| .004 | .7914 | .9257 | .999800 | -5. |
| .005 | .7720 | .9183 | .999752 | -7. |
| .006 | .7552 | .9118 | .999704 | -9. |
| .007 | .7403 | .9059 | .999657 | -11. |
| .008 | .7269 | .9007 | .999611 | -13. |
| .009 | .7148 | .8958 | .999564 | -15. |
| .010 | .7037 | .8913 | .999518 | -18. |
| .020 | .6248 | .8588 | .999072 | -49. |
| .030 | .5753 | .8377 | .998643 | -87. |
| .040 | .5396 | .8225 | .998224 | -131. |
| .050 | .5120 | .8109 | .997811 | -179. |
| .060 | .4898 | .8019 | .997403 | -230. |
| .070 | .4715 | .7949 | .996997 | -285. |
| .080 | .4562 | .7896 | .996592 | -342. |
| .090 | .4432 | .7857 | .996185 | -401. |
| .100 | .4321 | .7830 | .995777 | -463. |

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln\gamma)$ | $\sigma(\gamma)$ |
|-----------------------------------|----------------|---------------------|------------------|
| .001 | .0001 | .0002 | .0002 |
| .010 | .0004 | .0011 | .0008 |
| .100 | .0004 | .0013 | .0006 |

Coefficients of Correlating Equations

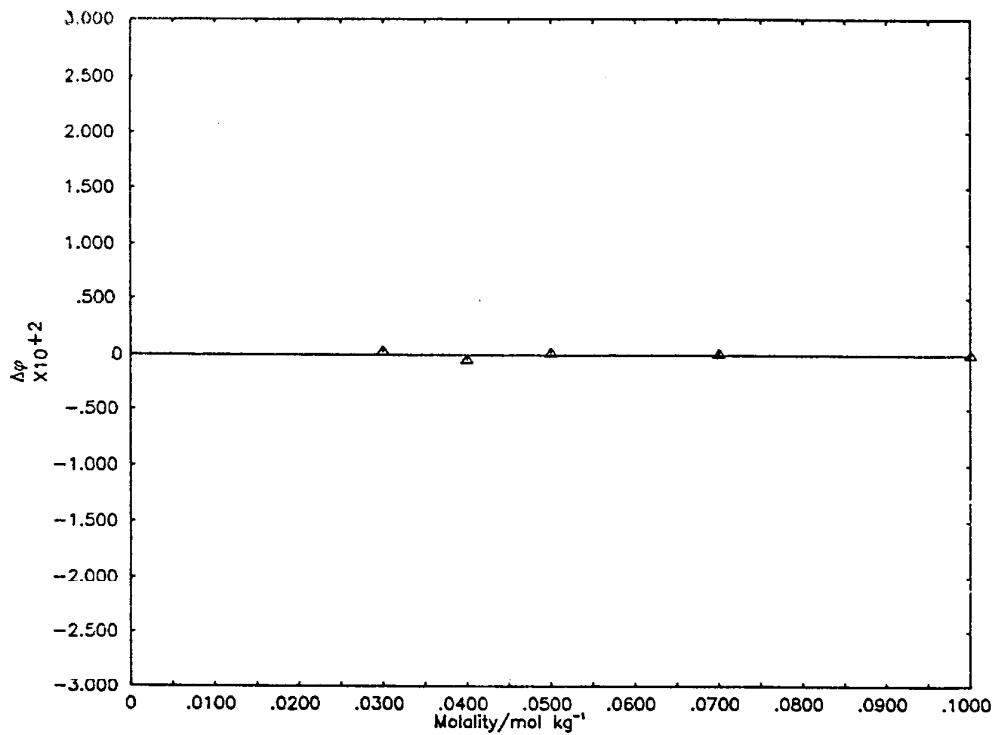
| Eqs 1 | | Eqs 2 | | Eqs 3 | | |
|-------|-----------------|------------------------|-----------------|------------------------|-----------------|------------------------|
| Par | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ |
| 1 | .9950357293+00 | .913-01 | -.3331776014+01 | .203+00 | -.5465733752+01 | .895-01 |
| 2 | -.4202846401+00 | .370+00 | .1491412062+02 | .603+00 | -.3231087553+01 | .266+00 |
| 3 | .3682235684+01 | .113+01 | | | | |

$$\begin{aligned}\sigma(\text{eqs 1}) &= .393-03 \\ \sigma(\text{eqs 2}) &= .236-02 \\ \sigma(\text{eqs 3}) &= .104-02\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Berka and Masterton [12]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_C data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\phi_{298.15}$ |
|-----------------------------------|-----------------|
| .030000 | .8380 |
| .040000 | .8220 |
| .050000 | .8110 |
| .070000 | .7950 |
| .100000 | .7830 |



Deviation Plot For $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}]_2$: $\Delta\phi$ vs molality

▲ Berka and Masterton [12] - vapor pressure osmometry

[Co(NH₃)₅CH₃COO]Br₂Recommend Values for the mean activity and osmotic coefficient of [Co(NH₃)₅CH₃COO]Br₂ in H₂O at 298.15 K

| <i>m/mol·kg</i> ⁻¹ | <i>γ</i> | <i>φ</i> | <i>a_w</i> | <i>ΔG^{ex}/J·kg</i> ⁻¹ |
|-------------------------------|----------|----------|----------------------|---|
| .001 | .8848 | .9602 | .999948 | -1. |
| .002 | .8440 | .9454 | .999898 | -2. |
| .003 | .8149 | .9347 | .999848 | -3. |
| .004 | .7919 | .9260 | .999800 | -5. |
| .005 | .7726 | .9187 | .999752 | -7. |
| .006 | .7559 | .9122 | .999704 | -9. |
| .007 | .7411 | .9065 | .999657 | -11. |
| .008 | .7279 | .9013 | .999610 | -13. |
| .009 | .7158 | .8965 | .999564 | -15. |
| .010 | .7042 | .8921 | .999518 | -18. |
| .020 | .6263 | .8598 | .999071 | -49. |
| .030 | .5768 | .8385 | .998641 | -87. |
| .040 | .5407 | .8226 | .998223 | -130. |
| .050 | .5124 | .8098 | .997814 | -178. |
| .060 | .4892 | .7592 | .997412 | -229. |
| .070 | .4657 | .7901 | .997015 | -284. |
| .080 | .4529 | .7822 | .996624 | -342. |
| .090 | .4381 | .7752 | .996237 | -402. |
| .100 | .4250 | .7689 | .995853 | -464. |
| .200 | .3426 | .7276 | .992166 | -1188. |
| .300 | .2980 | .7036 | .988659 | -2040. |
| .400 | .2681 | .6659 | .985282 | -2981. |
| .500 | .2460 | .6715 | .982018 | -3993. |
| .600 | .2286 | .6589 | .978860 | -5064. |

| <i>m/mol·kg</i> ⁻¹ | <i>σ(φ)</i> | <i>σ(z_{ny})</i> | <i>σ(γ)</i> |
|-------------------------------|-------------|--------------------------|-------------|
| .001 | .0000 | .0001 | .0001 |
| .010 | .0002 | .0005 | .0004 |
| .100 | .0006 | .0019 | .0008 |
| .600 | .0011 | .0022 | .0005 |

Coefficients of Correlating Equations

| | Eqs 1 | | | Eqs 2 | | |
|-----|-----------------|----------|-----------------|----------|-----------------|----------|
| Par | coefficients | σ(coeff) | coefficients | σ(coeff) | coefficients | σ(coeff) |
| 1 | .9878033191+00 | .179-01 | -.4217930037+01 | .259+00 | .5966862035+01 | .316-01 |
| 2 | -.1935269567+00 | .410-01 | .2351029944+02 | .131+01 | -.6144418679+01 | .893-01 |
| 3 | -.6819375294-02 | .350-01 | -.2400114309+02 | .225+01 | .2649536945+01 | .668-01 |
| 4 | | | .1047111653+02 | .127+01 | | |

$\sigma(\text{eqs 1}) = .125-02$

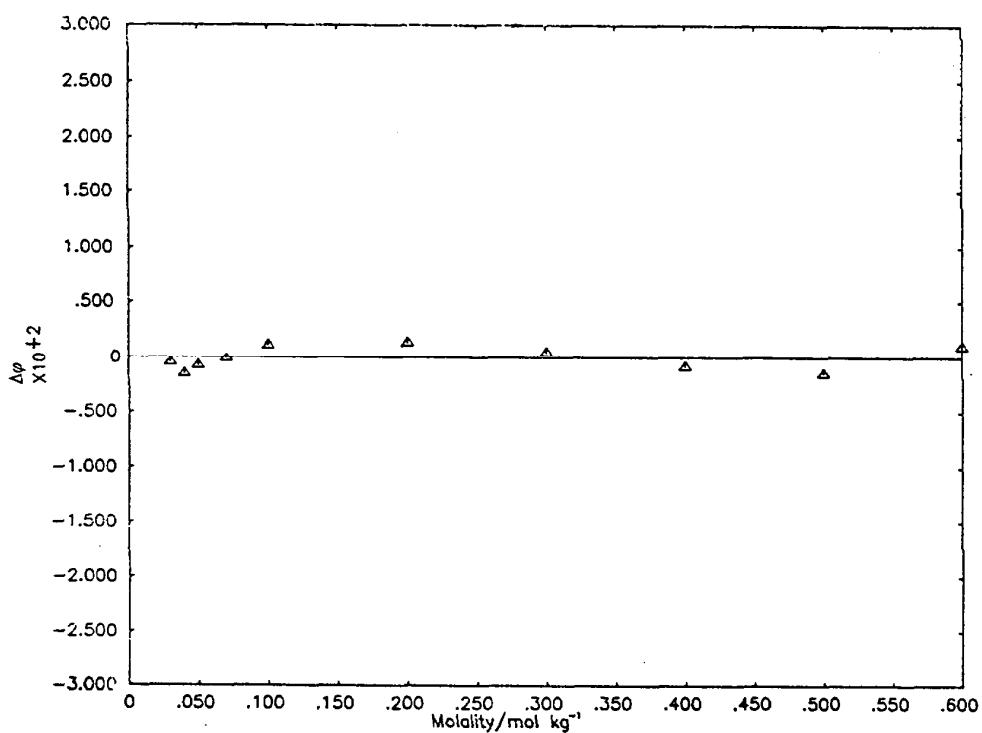
$\sigma(\text{eqs 2}) = .245-02$

$\sigma(\text{eqs 3}) = .786-03$

Experimental Data Employed in Generation of Correlating Equations

Berka and Masterton [12]. Vapor pressure osmometry measurements performed at 37°C. φ_L and φ_C data for CoCl₂ were used to adjust this data to 25°C. Assigned weight is 1.0.

| <i>m/mol·kg</i> ⁻¹ | <i>φ_{298.15}</i> |
|-------------------------------|---------------------------|
| .030000 | .8380 |
| .040000 | .8210 |
| .050000 | .8090 |
| .070000 | .7900 |
| .100000 | .7700 |
| .200000 | .7290 |
| .300000 | .7040 |
| .400000 | .6850 |
| .500000 | .6700 |
| .600000 | .6600 |



Deviation Plot For $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}]\text{Br}_2$: $\Delta\phi$ vs molality

▲ Berka and Masterton [12] - vapor pressure osmometry

$$[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}]\text{Cl}_2$$

Recommended Values for the mean activity and osmotic coefficient of $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}]\text{Cl}_2$ 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 | .8830 | .9593 | .999948 | -1. |
| .002 | .8409 | .9437 | .999898 | -2. |
| .003 | .8107 | .9323 | .999849 | -3. |
| .004 | .7867 | .9230 | .999800 | -5. |
| .005 | .7665 | .9150 | .999753 | -7. |
| .006 | .7490 | .9080 | .999706 | -9. |
| .007 | .7335 | .9018 | .999659 | -11. |
| .008 | .7196 | .8961 | .999613 | -13. |
| .009 | .7069 | .8909 | .999567 | -16. |
| .010 | .6953 | .8861 | .999521 | -19. |
| .020 | .6132 | .8512 | .999080 | -51. |
| .030 | .5619 | .8287 | .998657 | -90. |
| .040 | .5250 | .8124 | .998245 | -136. |
| .050 | .4966 | .7999 | .997841 | -186. |
| .060 | .4736 | .7900 | .997442 | -240. |
| .070 | .4545 | .7818 | .997047 | -297. |
| .080 | .4382 | .7749 | .996655 | -357. |
| .090 | .4241 | .7691 | .996266 | -421. |
| .100 | .4117 | .7640 | .995879 | -484. |
| .200 | .3349 | .7320 | .992118 | -1229. |
| .300 | .2919 | .7079 | .988588 | -2096. |
| .400 | .2615 | .6852 | .985296 | -3054. |
| .500 | .2396 | .6699 | .982059 | -4085. |
| .600 | .2260 | .6710 | .978456 | -5171. |

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln\gamma)$ | $\sigma(\gamma)$ |
|-----------------------------------|----------------|---------------------|------------------|
| .001 | .0001 | .0002 | .0002 |
| .010 | .0007 | .0015 | .0011 |
| .100 | .0020 | .0059 | .0024 |
| .600 | .0162 | .0304 | .0069 |

Coefficients of Correlating Equations

| Par | Eqs 1 | | Eqs 2 | | Eqs 3 | |
|-----|-----------------|------------------------|-----------------|------------------------|-----------------|------------------------|
| | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ |
| 1 | .9220308995-01 | .423+00 | -.9298519237+01 | .589+00 | .2749348039+01 | .348+00 |
| 2 | .3809046170+01 | .276+01 | .5635548423+02 | .434+01 | .1287122212+02 | .256+01 |
| 3 | -.4474150070+01 | .109+01 | -.1059265592+03 | .121+02 | -.4104642937+02 | .713+01 |
| 4 | .2993927293+01 | .595+00 | .1010399493+03 | .147+02 | .4469339082+02 | .868+01 |
| 5 | | | -.3705374752+02 | .657+01 | -.1692672194+02 | .388+01 |

$$\sigma(\text{eqs 1}) = .263-02$$

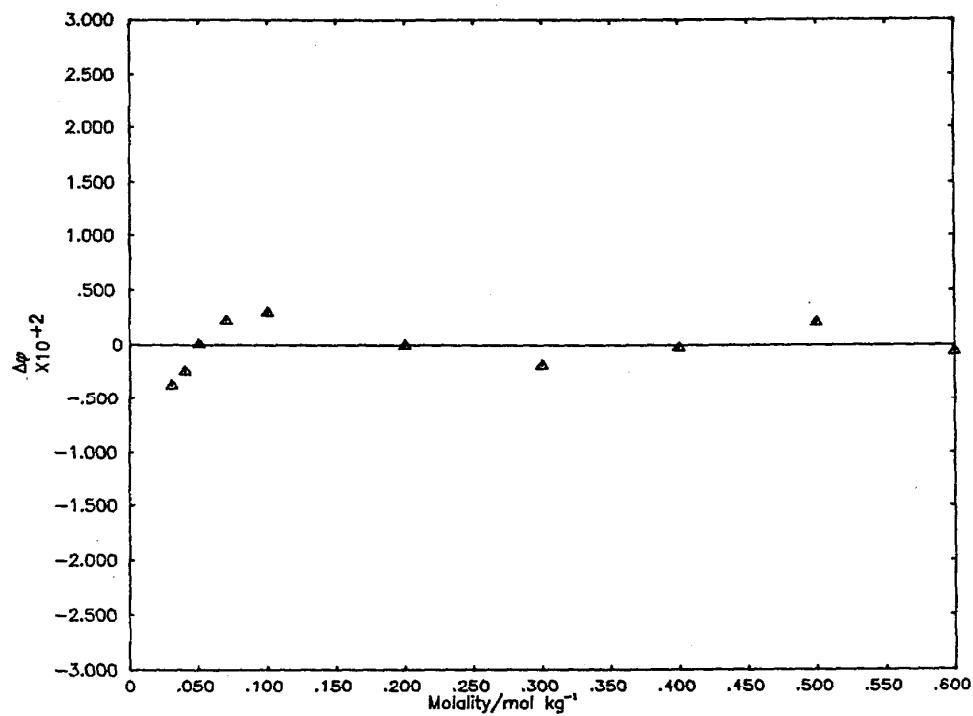
$$\sigma(\text{eqs 2}) = .194-02$$

$$\sigma(\text{eqs 3}) = .115-02$$

Experimental Data Employed in Generation of Correlating Equations

Berka and Masterton [12]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_C data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\phi_{298.15}$ |
|-----------------------------------|-----------------|
| .030000 | .8250 |
| .040000 | .8100 |
| .050000 | .8000 |
| .070000 | .7840 |
| .100000 | .7670 |
| .200000 | .7320 |
| .300000 | .7060 |
| .400000 | .6850 |
| .500000 | .6720 |
| .600000 | .6710 |



Deviation Plot For $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}]\text{Cl}_2$: $\Delta\phi$ vs molality

▲ Berka and Masterton [12] - vapor pressure osmometry

$$[\text{Co}(\text{NH}_3)_5(\text{CH}_3)_2\text{CHCOO}](\text{NO}_3)_2$$

Recommended Values for the mean activity and osmotic coefficient of $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)_2\text{CHCOO}](\text{NO}_3)_2$ 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 | .8841 | .9555 | .999948 | -1. |
| .002 | .8427 | .9447 | .999898 | -2. |
| .003 | .8132 | .9337 | .999849 | -3. |
| .004 | .7897 | .9247 | .999800 | -5. |
| .005 | .7700 | .9170 | .999752 | -7. |
| .006 | .7529 | .9103 | .999705 | -9. |
| .007 | .7377 | .9043 | .999658 | -11. |
| .008 | .7241 | .8988 | .999611 | -13. |
| .009 | .7117 | .8937 | .999565 | -16. |
| .010 | .7003 | .8890 | .999520 | -18. |
| .020 | .6191 | .8643 | .999077 | -50. |
| .030 | .5675 | .8310 | .998654 | -89. |
| .040 | .5296 | .8131 | .998244 | -133. |
| .050 | .4998 | .7986 | .997844 | -183. |
| .060 | .4754 | .7863 | .997453 | -236. |
| .070 | .4548 | .7757 | .997070 | -293. |
| .080 | .4369 | .7663 | .996692 | -354. |
| .090 | .4213 | .7579 | .996320 | -416. |
| .100 | .4074 | .7502 | .995953 | -482. |
| .200 | .3194 | .6979 | .992484 | -1248. |
| .300 | .2718 | .6654 | .989269 | -2160. |
| .400 | .2401 | .6411 | .986237 | -3177. |
| .500 | .2168 | .6213 | .983352 | -4277. |
| .600 | .1986 | .6044 | .980593 | -5447. |
| .700 | .1839 | .5895 | .977945 | -6679. |
| .800 | .1716 | .5762 | .975394 | -7964. |
| .900 | .1612 | .5642 | .972929 | -9298. |
| 1.000 | .1522 | .5533 | .970540 | -10677. |
| 1.250 | .1342 | .5299 | .964831 | -14297. |
| 1.500 | .1208 | .5115 | .959384 | -18132. |
| 1.750 | .1103 | .4973 | .954056 | -22149. |
| 2.000 | .1020 | .4871 | .948711 | -26322. |
| 2.250 | .0954 | .4807 | .943215 | -30629. |
| 2.500 | .0901 | .4782 | .937436 | -35053. |

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln y)$ | $\sigma(\gamma)$ |
|-----------------------------------|----------------|-----------------|------------------|
| .001 | .0000 | .0001 | .0001 |
| .010 | .0004 | .0008 | .0006 |
| .100 | .0015 | .0040 | .0016 |
| 1.000 | .0022 | .0063 | .0010 |
| 2.000 | .0025 | .0063 | .0006 |
| 2.500 | .0041 | .0078 | .0007 |

Coefficients of Correlating Equations

| | <u>Eqs 1</u> | | <u>Eqs 2</u> | | <u>Eqs 3</u> | |
|-----|-----------------|------------------------|-----------------|------------------------|-----------------|------------------------|
| Par | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ |
| 1 | .8912538286+00 | .190-01 | -.5464119350+01 | .410+00 | .5258751480+01 | .105+00 |
| 2 | -.3250277045+00 | .230-01 | .2942187474+02 | .215+01 | -.5345480272+01 | .253+00 |
| 3 | .4444344419-01 | .569-02 | -.4063296042+02 | .456+01 | .2865204740+01 | .211+00 |
| 4 | | | .3433603266+02 | .470+01 | -.5967808584+00 | .582-01 |
| 5 | | | -.1506417406+02 | .234+01 | | |
| 6 | | | .2646021998+01 | .451+00 | | |

$$\begin{aligned}\sigma(\text{eqs 1}) &= .452-02 \\ \sigma(\text{eqs 2}) &= .452-02 \\ \sigma(\text{eqs 3}) &= .454-02\end{aligned}$$

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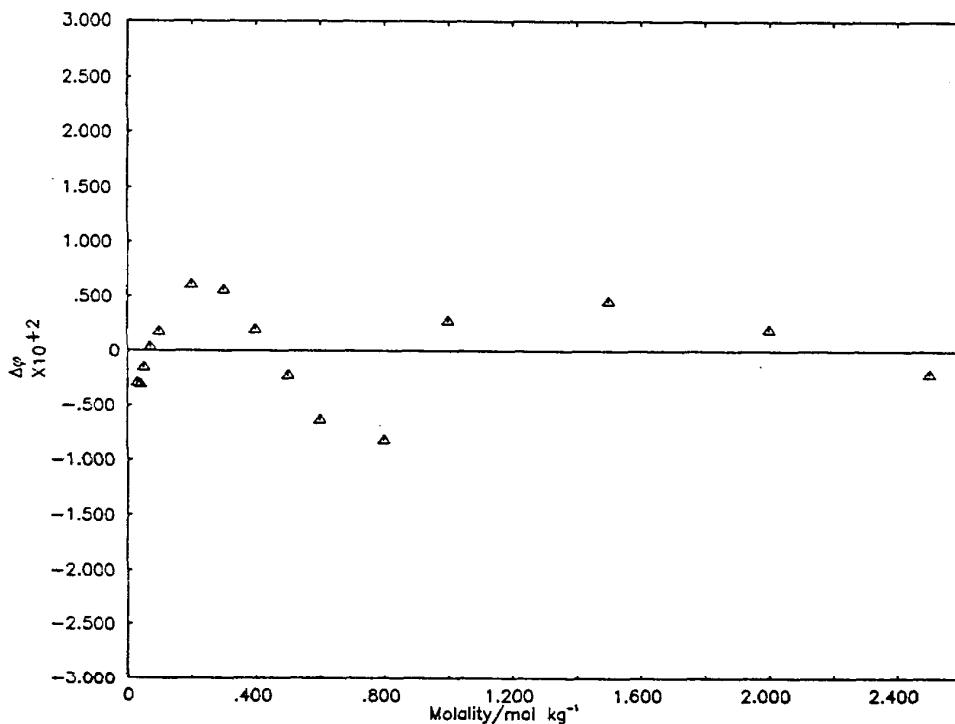
Experimental Data Employed in Generation of Correlating Equations

Berka and Masterton [12]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_c data for $\text{Co}(\text{NH}_3)_5(\text{CH}_3)_2\text{CHCOO}(\text{NO}_3)_2$ were used to adjust this data to 25°C. Assigned weight is 1.0

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\phi_{298.15}$ |
|-----------------------------------|-----------------|
| .030000 | .8280 |
| .040000 | .8100 |
| .050000 | .7970 |
| .070000 | .7760 |
| .100000 | .7520 |
| .200000 | .7040 |
| .300000 | .6710 |
| .400000 | .6430 |
| .500000 | .6190 |
| .600000 | .5980 |
| .800000 | .5680 |
| 1.000000 | .5560 |
| 1.500000 | .5160 |
| 2.000000 | .4890 |
| 2.500000 | .4760 |

Comments

The fit using equations 2 is difficult for this system.



Deviation Plot For $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)_2\text{CHCOO}](\text{NO}_3)_2$: $\Delta\phi$ vs molality

▲ Berka and Masterton [12] - vapor pressure osmometry

$$[\text{Co}(\text{NH}_3)_5(\text{CH}_3)_2\text{CHCOO}]_2$$

Recommended Values for the mean activity and osmotic coefficient of $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)_2\text{CHCOO}]_2$ 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 | .8844 | .9600 | .999948 | -1. |
| .002 | .8432 | .9450 | .999898 | -2. |
| .003 | .8140 | .9241 | .999849 | -3. |
| .004 | .7907 | .9053 | .999860 | -5. |
| .005 | .7712 | .8978 | .999752 | -7. |
| .006 | .7543 | .8913 | .999705 | -9. |
| .007 | .7394 | .8854 | .999658 | -11. |
| .008 | .7255 | .8801 | .999611 | -13. |
| .009 | .7138 | .8852 | .999565 | -16. |
| .010 | .7026 | .8807 | .999519 | -18. |
| .020 | .6232 | .8577 | .999073 | -49. |
| .030 | .5732 | .8361 | .998645 | -88. |
| .040 | .5368 | .8199 | .998229 | -131. |
| .050 | .5083 | .8070 | .997822 | -180. |
| .060 | .4850 | .7963 | .997421 | -232. |
| .070 | .4664 | .7871 | .997027 | -287. |
| .080 | .4485 | .7791 | .996637 | -346. |
| .090 | .4337 | .7720 | .996252 | -407. |
| .100 | .4206 | .7656 | .995871 | -470. |
| .200 | .3369 | .7213 | .992233 | -1204. |
| .300 | .2901 | .6906 | .988865 | -2071. |
| .400 | .2575 | .6643 | .985742 | -3037. |
| .500 | .2329 | .6414 | .982816 | -4084. |
| .600 | .2139 | .6232 | .979993 | -5200. |
| .700 | .1993 | .6117 | .977124 | -6374. |
| .800 | .1887 | .6092 | .974005 | -7595. |

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln\gamma)$ | $\sigma(\gamma)$ |
|-----------------------------------|----------------|---------------------|------------------|
| .001 | .0000 | .0001 | .0001 |
| .010 | .0002 | .0004 | .0003 |
| .100 | .0004 | .0013 | .0005 |
| .800 | .0008 | .0015 | .0003 |

Coefficients of Correlating Equations

| Par | Eqs 1 | | Eqs 2 | | Eqs 3 | |
|-----|-----------------|------------------------|-----------------|------------------------|-----------------|------------------------|
| | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ |
| 1 | .8548590270+00 | .188-01 | -.5735326414+01 | .309+00 | .5905619652+01 | .141-01 |
| 2 | .2002751341+00 | .600-01 | .3391495217+02 | .206+01 | -.6160048487+01 | .340-01 |
| 3 | -.9187716168+00 | .855-01 | -.5182782126+02 | .514+01 | .25925633302+01 | .218-01 |
| 4 | .6412327723+00 | .507-01 | .4264462977+02 | 1.558+01 | | |
| 5 | | | -.1365531608+02 | .221+01 | | |

$$\sigma(\text{eqs 1}) = .810-03$$

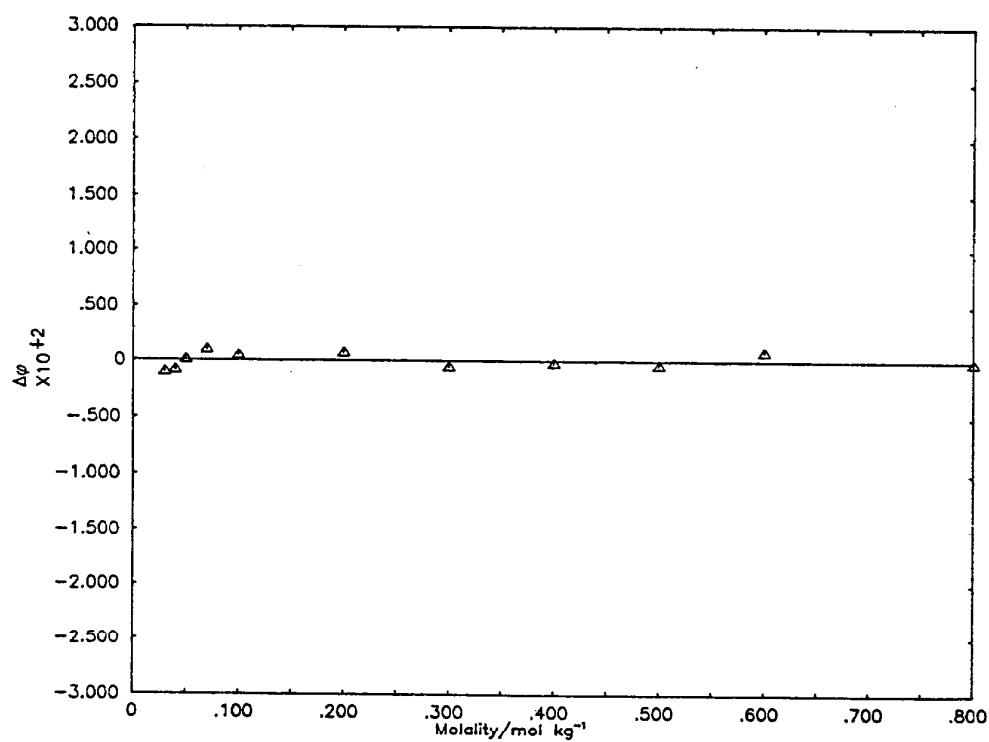
$$\sigma(\text{eqs 2}) = .151-02$$

$$\sigma(\text{eqs 3}) = .467-03$$

Experimental Data Employed in Generation of Correlating Equations

Berka and Masterton [12]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_c data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\phi_{298.15}$ |
|-----------------------------------|-----------------|
| .030000 | .8350 |
| .040000 | .8190 |
| .050000 | .8070 |
| .070000 | .7880 |
| .100000 | .7660 |
| .200000 | .7220 |
| .300000 | .6900 |
| .400000 | .6640 |
| .500000 | .6410 |
| .600000 | .6240 |
| .800000 | .6090 |



Deviation Plot For $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)_2\text{CHCOO}]_{\text{I}}_2$: $\Delta\phi$ vs molality

Δ Berka and Masterton [12] - vapor pressure osmometry

$$[\text{Co}(\text{NH}_3)_5(\text{CH}_3)_2\text{CHCOO}]\text{Br}_2$$

Recommended Values for the mean activity and osmotic coefficient of $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)_2\text{CHCOO}]\text{Br}_2$ 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 | .8835 | .9595 | .999948 | -1. |
| .002 | .8416 | .9441 | .999898 | -2. |
| .003 | .8117 | .9329 | .999849 | -3. |
| .004 | .7879 | .9237 | .999800 | -5. |
| .005 | .7679 | .9159 | .999753 | -7. |
| .006 | .7506 | .9090 | .999705 | -9. |
| .007 | .7352 | .9028 | .999658 | -11. |
| .008 | .7214 | .8972 | .999612 | -13. |
| .009 | .7089 | .8921 | .999566 | -16. |
| .010 | .6974 | .8873 | .999521 | -18. |
| .020 | .6157 | .8525 | .999079 | -50. |
| .030 | .5642 | .8297 | .998656 | -90. |
| .040 | .5270 | .8128 | .998244 | -135. |
| .050 | .4980 | .7995 | .997842 | -185. |
| .060 | .4745 | .7886 | .997446 | -238. |
| .070 | .4548 | .7795 | .997055 | -295. |
| .080 | .4379 | .7717 | .996669 | -355. |
| .090 | .4233 | .7650 | .996286 | -418. |
| .100 | .4103 | .7590 | .995906 | -483. |
| .200 | .3302 | .7219 | .992227 | -1234. |
| .300 | .2870 | .6550 | .988731 | -2113. |
| .400 | .2574 | .6794 | .985421 | -3082. |
| .500 | .2351 | .6620 | .982269 | -4127. |
| .600 | .2178 | .6487 | .979183 | -5233. |
| .700 | .2049 | .6424 | .975991 | -6390. |
| .800 | .1962 | .6463 | .972442 | -7587. |
| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln\gamma)$ | $\sigma(\gamma)$ | |
| .001 | .0001 | .0001 | .0001 | |
| .010 | .0004 | .0009 | .0006 | |
| .100 | .0008 | .0027 | .0011 | |
| .800 | .0018 | .0032 | .0006 | |

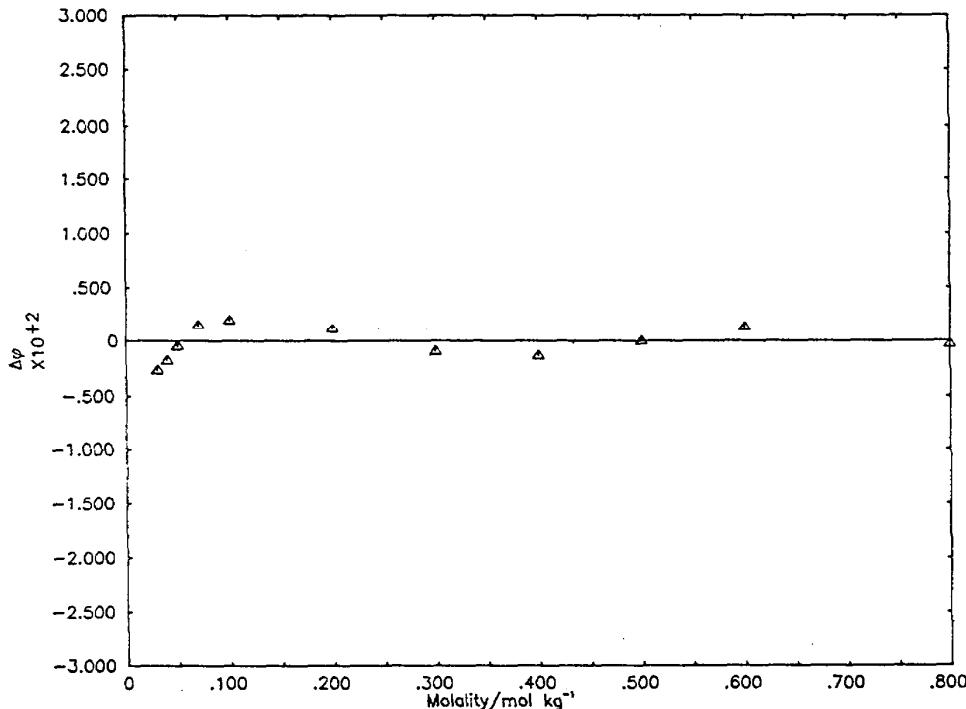
Coefficients of Correlating Equations

| | <u>Eqs 1</u> | | <u>Eqs 2</u> | | <u>Eqs 3</u> | |
|------|--------------------|--|----------------------------------|--|--------------------|--|
| Par. | <u>coefficient</u> | <u>$\sigma(\text{coeff})$</u> | <u>coefficient</u> | <u>$\sigma(\text{coeff})$</u> | <u>coefficient</u> | <u>$\sigma(\text{coeff})$</u> |
| 1 | .5675899742+00 | .465-01 | -.7259326751+01 | .429+00 | .4884191854+01 | .111+00 |
| 2 | .1073639410+01 | .191+00 | .4113308788+02 | .286+01 | -.2507992432+01 | .482+00 |
| 3 | -.1612047846+01 | .224+00 | -.6543484359+02 | .714+01 | -.1772302768+01 | .718+00 |
| 4 | .9438071158+00 | .124+00 | .5471241288+02 | .775+01 | .1810640513+01 | .353+00 |
| | | | -.177257511+02 | .307+01 | | |
| | | | $\sigma(\text{eqs 1}) = .179-02$ | | | |
| | | | $\sigma(\text{eqs 2}) = .210-02$ | | | |
| | | | $\sigma(\text{eqs 3}) = .148-02$ | | | |

Experimental Data Employed in Generation of Correlating Equations

Berka and Masterton [12]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_C data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\phi_{298.15}$ |
|-------------------------------------|-----------------|
| .030000 | .8270 |
| .040000 | .8110 |
| .050000 | .7990 |
| .070000 | .7810 |
| .100000 | .7610 |
| .200000 | .7230 |
| .300000 | .6980 |
| .400000 | .6780 |
| .500000 | .6620 |
| .600000 | .6500 |
| .800000 | .6460 |



Deviation Plot For $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)_2\text{CHCOO}] \text{Br}_2$: $\Delta\phi$ vs molality

▲ Berka and Masterton [12] - vapor pressure osmometry

$$[\text{Co}(\text{NH}_3)_5(\text{CH}_3)_2\text{CHCOO}\text{Cl}_2]$$

Recommended Values for the mean activity and osmotic coefficient of $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)_2\text{CHCOO}\text{Cl}_2]$ 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 | .8844 | .9600 | .999948 | -1. |
| .002 | .8433 | .9451 | .999898 | -2. |
| .003 | .8141 | .9342 | .999849 | -3. |
| .004 | .7908 | .9254 | .999800 | -5. |
| .005 | .7713 | .9179 | .999752 | -7. |
| .006 | .7544 | .9113 | .999705 | -9. |
| .007 | .7395 | .9055 | .999658 | -11. |
| .008 | .7261 | .9001 | .999611 | -13. |
| .009 | .7139 | .8952 | .999565 | -16. |
| .010 | .7027 | .8907 | .999519 | -18. |
| .020 | .6233 | .8577 | .999073 | -49. |
| .030 | .5733 | .8360 | .998645 | -88. |
| .040 | .5368 | .8199 | .998229 | -131. |
| .050 | .5084 | .8070 | .997822 | -180. |
| .060 | .4852 | .7964 | .997421 | -232. |
| .070 | .4656 | .7874 | .997025 | -287. |
| .080 | .4489 | .7797 | .996634 | -345. |
| .090 | .4343 | .7730 | .996247 | -406. |
| .100 | .4214 | .7670 | .995863 | -469. |
| .200 | .3414 | .7308 | .992131 | -1198. |
| .300 | .2998 | .7139 | .988492 | -2049. |
| .400 | .2732 | .7045 | .984884 | -2981. |
| .500 | .2542 | .6991 | .981285 | -3974. |
| .600 | .2398 | .6960 | .977683 | -5015. |
| .700 | .2284 | .6944 | .974073 | -6095. |
| .800 | .2191 | .6937 | .970452 | -7209. |
| .900 | .2114 | .6937 | .966820 | -8352. |
| 1.000 | .2048 | .6942 | .963175 | -9519. |
| 1.250 | .1918 | .6969 | .954012 | -12531. |
| 1.500 | .1823 | .7007 | .944781 | -15650. |
| 1.750 | .1749 | .7050 | .935491 | -18855. |
| 2.000 | .1690 | .7097 | .926152 | -22130. |
| 2.250 | .1641 | .7146 | .916774 | -25463. |
| 2.500 | .1601 | .7194 | .907367 | -28647. |

| $m/\text{mol}\cdot\text{kg}^{-1}$ | $\sigma(\phi)$ | $\sigma(\ln\gamma)$ | $\sigma(\gamma)$ |
|-----------------------------------|----------------|---------------------|------------------|
| .001 | .0000 | .0001 | .0001 |
| .010 | .0002 | .0005 | .0003 |
| .100 | .0011 | .0027 | .0011 |
| 1.000 | .0017 | .0067 | .0014 |
| 2.000 | .0027 | .0068 | .0011 |
| 2.500 | .0037 | .0071 | .0011 |

Coefficients of Correlating Equations

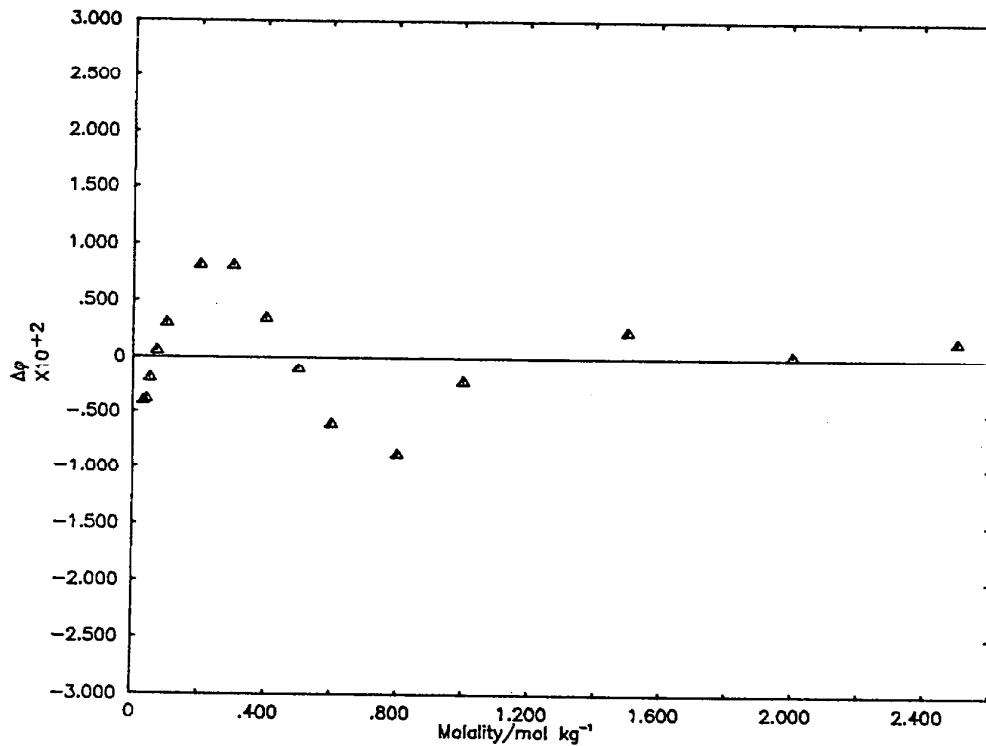
| Par | Eqs 1 | | Eqs 2 | | Eqs 3 | |
|-----|----------------|------------------------|-----------------|------------------------|-----------------|------------------------|
| | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ |
| 1 | .8911348290+00 | .100-01 | -.5354876648+01 | .385+00 | .5141661184+01 | .179+00 |
| 2 | .1618118279-01 | .535-02 | -.3079356425+02 | .202+01 | -.1954961021+01 | .940+00 |
| 3 | | | -.4357612886+02 | .427+01 | -.5737694200+01 | .199+01 |
| 4 | | | .3718596848+02 | .441+01 | .9216594472+01 | .205+01 |
| 5 | | | -.1640013614+02 | .220+01 | -.5250304976+01 | .102+01 |
| 6 | | | .2888405746+01 | .423+00 | .1064547987+01 | .197+00 |

$$\begin{aligned}\sigma(\text{eqs 1}) &= .492-02 \\ \sigma(\text{eqs 2}) &= .424-02 \\ \sigma(\text{eqs 3}) &= .197-02\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Berka and Masterton [12]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_c data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\phi_{298.15}$ |
|-------------------------------------|-----------------|
| .030000 | .8320 |
| .040000 | .8160 |
| .050000 | .8050 |
| .070000 | .7880 |
| .100000 | .7700 |
| .200000 | .7390 |
| .300000 | .7220 |
| .400000 | .7080 |
| .500000 | .6980 |
| .600000 | .6900 |
| .800000 | .6850 |
| 1.000000 | .6920 |
| 1.500000 | .7030 |
| 2.000000 | .7100 |
| 2.500000 | .7210 |



Deviation Plot For $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)_2\text{CHCOO}]\text{Cl}_2$: $\Delta\phi$ vs molality

▲ Berka and Masterton [12] - vapor pressure osmometry

trans-[Co(C₂H₈N₂)NH₃NO₂](NO₃)₂

Recommended Values for the mean activity and osmotic coefficient of
trans-[Co(C₂H₈N₂)NH₃NO₂]₂(NO₃)₂ in H₂O at 298.15 K

| <i>m/mol·kg⁻¹</i> | <i>γ</i> | <i>φ</i> | <i>a_w</i> | <i>ΔG^{ex}/J·kg⁻¹</i> |
|------------------------------|----------|----------|----------------------|--|
| .001 | .8842 | .9599 | .999948 | -1. |
| .002 | .8429 | .9449 | .999898 | -2. |
| .003 | .8135 | .9338 | .999849 | -3. |
| .004 | .7901 | .9249 | .999800 | -5. |
| .005 | .7704 | .9173 | .999752 | -7. |
| .006 | .7533 | .9106 | .999705 | -9. |
| .007 | .7382 | .9045 | .999658 | -11. |
| .008 | .7246 | .8991 | .999611 | -13. |
| .009 | .7122 | .8940 | .999565 | -16. |
| .010 | .7009 | .8894 | .999519 | -18. |
| .020 | .6157 | .8547 | .999077 | -50. |
| .030 | .5680 | .8211 | .998653 | -89. |
| .040 | .5300 | .8130 | .998244 | -133. |
| .050 | .5000 | .7981 | .997846 | -163. |
| .060 | .4753 | .7854 | .997457 | -236. |
| .070 | .4543 | .7742 | .997075 | -293. |
| .080 | .4362 | .7643 | .996701 | -353. |
| .090 | .4202 | .7553 | .996333 | -417. |
| .100 | .4060 | .7471 | .995971 | -482. |
| .200 | .3145 | .6871 | .992601 | -1255. |
| .300 | .2636 | .6456 | .989587 | -2184. |
| .400 | .2291 | .6122 | .986853 | -3230. |
| .500 | .2036 | .5840 | .984343 | -4371. |
| .600 | .1839 | .5601 | .982002 | -5593. |
| .700 | .1682 | .5403 | .979765 | -6886. |
| .800 | .1556 | .5250 | .977557 | -8241. |

| <i>m/mol·kg⁻¹</i> | <i>σ(φ)</i> | <i>σ(lnγ)</i> | <i>σ(γ)</i> |
|------------------------------|-------------|---------------|-------------|
| .001 | .0000 | .0000 | .0000 |
| .010 | .0001 | .0002 | .0001 |
| .100 | .0002 | .0006 | .0002 |
| .800 | .0004 | .0007 | .0001 |

Coefficients of Correlating Equations

| Par | <u>Eqs 1</u> | | <u>Eqs 2</u> | | <u>Eqs 3</u> | |
|-----|-----------------|----------|-----------------|----------|-----------------|----------|
| | coefficients | σ(coeff) | coefficient | σ(coeff) | coefficient | σ(coeff) |
| 1 | .9410941796+00 | .861-02 | -.5469081010+01 | .167+00 | .6056465915+01 | .893-01. |
| 2 | -.5064808420+00 | .260-01 | .2973169058+02 | .111+01 | -.9687454751+01 | .595+00 |
| 3 | -.6893857214-01 | .391-01 | -.4205139785+02 | .278+01 | .1094825514+02 | .149+01 |
| 4 | .1402876903+00 | .236-01 | .3359673389+02 | .302+01 | -.7692814214+01 | .162+01 |
| 5 | | | -.1070282166+02 | .120+01 | .2475347024+01 | .640+00 |

$$\sigma(\text{eqs 1}) = .392-03$$

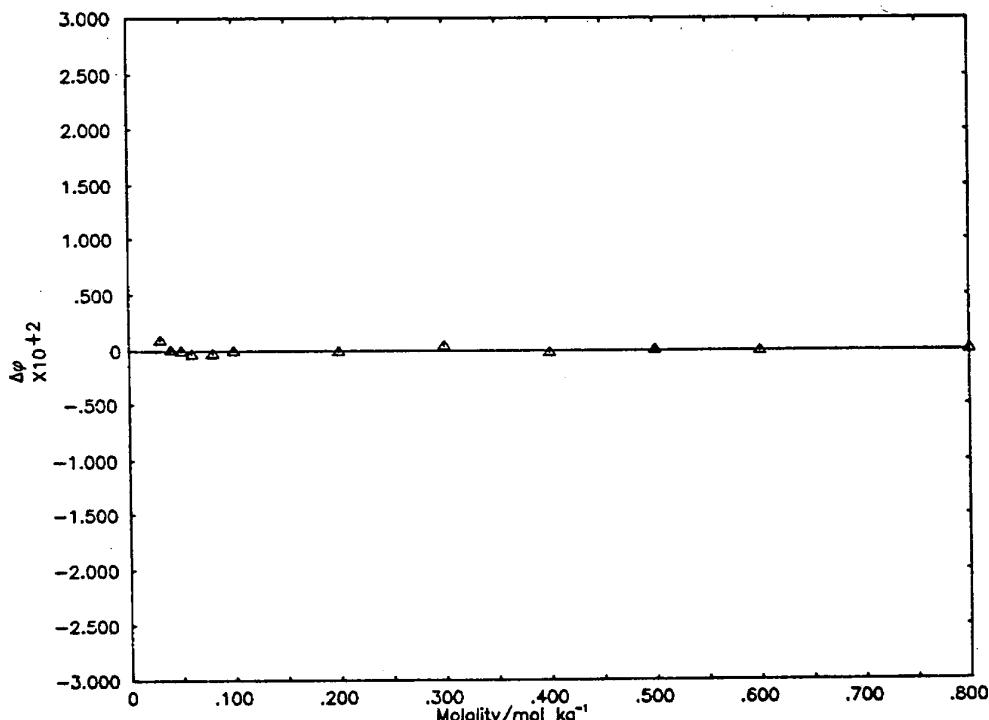
$$\sigma(\text{eqs 2}) = .830-03$$

$$\sigma(\text{eqs 3}) = .444-03$$

Experimental Data Employed in Generation of Correlating Equations

Masterton et al [21]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_c data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\phi_{298.15}$ |
|-------------------------------------|-----------------|
| .030000 | .8320 |
| .040000 | .8130 |
| .050000 | .7980 |
| .060000 | .7850 |
| .080000 | .7640 |
| .100000 | .7470 |
| .200000 | .6870 |
| .300000 | .6460 |
| .400000 | .6120 |
| .500000 | .5840 |
| .600000 | .5600 |
| .800000 | .5250 |



Deviation Plot For $\text{trans}-[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NH}_3\text{NO}_2]_2(\text{NO}_3)_2$: $\Delta\phi$ vs molality

▲ Masterton et al [21] - vapor pressure osmometry

trans-[Co(C₂H₈N₂)NH₃NO₂]I₂

Recommended Values for the mean activity and osmotic coefficient of trans-[Co(C₂H₈N₂)NH₃NO₂]I₂ in H₂O at 298.15 K

| <i>m/mol·kg⁻¹</i> | γ | ϕ | a_w | $\Delta G^{\text{ex}}/\text{J} \cdot \text{kg}^{-1}$ |
|------------------------------|----------|--------|---------|--|
| .001 | .8841 | .9599 | .999948 | -1. |
| .002 | .8429 | .9449 | .999898 | -2. |
| .003 | .8136 | .9240 | .999849 | -3. |
| .004 | .7903 | .9252 | .999800 | -5. |
| .005 | .7708 | .9177 | .999752 | -7. |
| .006 | .7539 | .9112 | .999705 | -9. |
| .007 | .7390 | .9054 | .999658 | -11. |
| .008 | .7257 | .9001 | .999611 | -13. |
| .009 | .7136 | .8953 | .999565 | -16. |
| .010 | .7025 | .8909 | .999519 | -18. |
| .020 | .6241 | .8590 | .999072 | -49. |
| .030 | .5750 | .8384 | .998642 | -87. |
| .040 | .5393 | .8220 | .998222 | -131. |
| .050 | .5113 | .8106 | .997812 | -179. |
| .060 | .4883 | .7599 | .997409 | -231. |
| .070 | .4686 | .7504 | .997014 | -285. |
| .080 | .4515 | .7817 | .996626 | -343. |
| .090 | .4362 | .7734 | .996245 | -404. |
| .100 | .4224 | .7655 | .995871 | -467. |
| .200 | .3267 | .6939 | .992527 | -1209. |
| .300 | .2719 | .6450 | .989596 | -2113. |

| <i>m/mol·kg⁻¹</i> | $\sigma(\phi)$ | $\sigma(\ln\gamma)$ | $\sigma(\gamma)$ |
|------------------------------|----------------|---------------------|------------------|
| .001 | .0001 | .0001 | .0001 |
| .010 | .0003 | .0006 | .0004 |
| .100 | .0003 | .0008 | .0003 |
| .300 | .0004 | .0011 | .0003 |

Coefficients of Correlating Equations

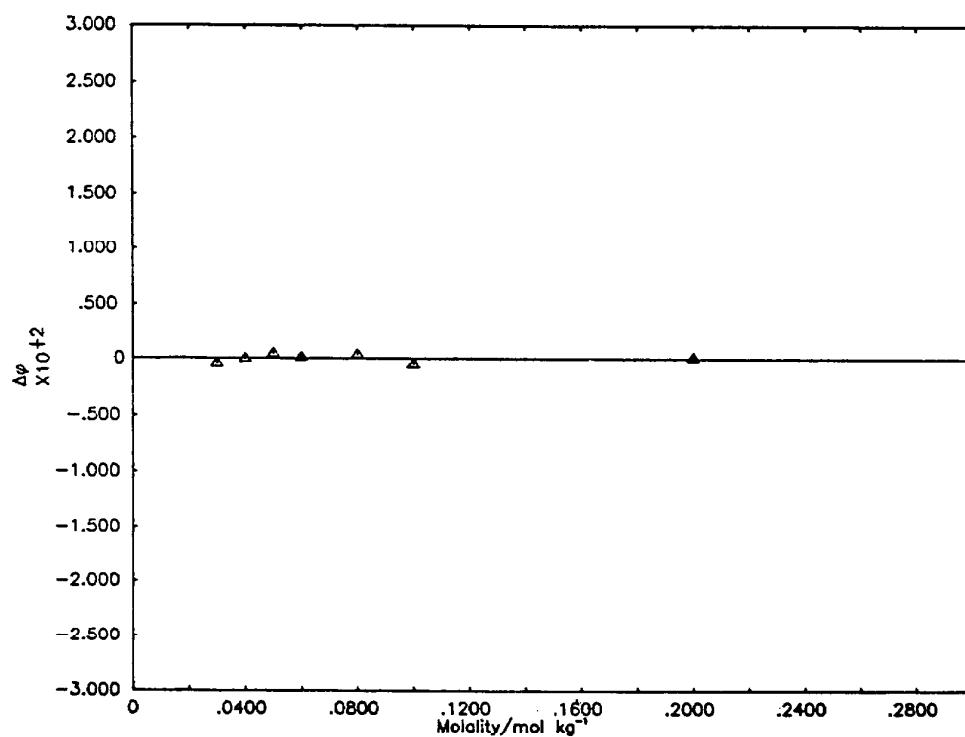
| | Eqs 1 | | | Eqs 2 | | |
|------|-----------------|------------------------|--|-----------------|------------------------|-----------------|
| Par. | coefficient | $\sigma(\text{coeff})$ | | coefficient | $\sigma(\text{coeff})$ | coefficient |
| 1 | .5030807927+00 | .702-01 | | -.6485233624+01 | .281+00 | .5518860419+01 |
| 2 | .2253042069+01 | .365+00 | | -.4175710165+02 | .195+01 | -.1268600177+00 |
| 3 | -.8961814962+01 | .760+00 | | -.7230488756+02 | .459+01 | -.181881629+02 |
| 4 | .1256280010+02 | .974+00 | | -.4961577283+02 | .358+01 | .1888478621+02 |

$$\begin{aligned}\sigma(\text{eqs 1}) &= .432-03 \\ \sigma(\text{eqs 2}) &= .850-03 \\ \sigma(\text{eqs 3}) &= .363-03\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Masterton et al [21]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_C data for CoCl₂ were used to adjust this data to 25°C. Assigned weight is 1.0.

| <i>m/mol·kg⁻¹</i> | $\phi_{298.15}$ |
|------------------------------|-----------------|
| .030000 | .6380 |
| .040000 | .8230 |
| .050000 | .8110 |
| .060000 | .8000 |
| .080000 | .7820 |
| .100000 | .7650 |
| .200000 | .6940 |
| .300000 | .6450 |



Deviation Plot For $\text{trans-}[\text{Co}(\text{C}_8\text{H}_8\text{N}_2)_2\text{NH}_3\text{NO}_2]\text{I}_2$: $\Delta\phi$ vs molality.

▲ Masterton et al [21] - vapor pressure osmometry

trans-[Co(C₂H₈N₂)NH₃NO₂]Br₂Recommended Values for the mean activity and osmotic coefficient of trans-[Co(C₂H₈N₂)NH₃NO₂]Br₂ in H₂O at 298.15 K

| <i>m/mol·kg⁻¹</i> | <i>γ</i> | <i>φ</i> | <i>a_w</i> | <i>ΔG^{ex/J·kg⁻¹}</i> |
|------------------------------|----------|----------|----------------------|--|
| .001 | .8844 | .9600 | .999948 | -1. |
| .002 | .8433 | .9461 | .999898 | -2. |
| .003 | .8141 | .9342 | .999849 | -3. |
| .004 | .7908 | .9253 | .999800 | -5. |
| .005 | .7712 | .9178 | .999752 | -7. |
| .006 | .7542 | .9111 | .999705 | -9. |
| .007 | .7392 | .9052 | .999658 | -11. |
| .008 | .7257 | .8998 | .999611 | -13. |
| .009 | .7135 | .8948 | .999565 | -16. |
| .010 | .7022 | .8902 | .999519 | -18. |
| .020 | .6218 | .8561 | .999075 | -49. |
| .030 | .5705 | .8330 | .998650 | -88. |
| .040 | .5328 | .8152 | .998239 | -132. |
| .050 | .5031 | .8006 | .997839 | -181. |
| .060 | .4786 | .7882 | .997447 | -234. |
| .070 | .4578 | .7774 | .997063 | -291. |
| .080 | .4395 | .7677 | .996686 | -350. |
| .090 | .4240 | .7589 | .996315 | -413. |
| .100 | .4099 | .7509 | .995950 | -478. |
| .200 | .3195 | .6536 | .992531 | -1242. |
| .300 | .2695 | .6554 | .989430 | -2156. |
| .400 | .2359 | .6257 | .986563 | -3183. |
| .500 | .2112 | .6012 | .983884 | -4299. |
| .600 | .1920 | .5804 | .981356 | -5492. |
| .700 | .1765 | .5624 | .978949 | -6751. |
| .800 | .1637 | .5467 | .976640 | -8069. |
| .900 | .1530 | .5330 | .974405 | -9440. |
| 1.000 | .1438 | .5212 | .972226 | -10860. |
| 1.250 | .1260 | .4980 | .966915 | -14593. |
| 1.500 | .1130 | .4825 | .961643 | -18549. |
| 1.750 | .1032 | .4726 | .956281 | -22689. |
| 2.000 | .0956 | .4670 | .950777 | -26984. |
| 2.250 | .0895 | .4639 | .945147 | -31410. |
| 2.400 | .0864 | .4627 | .941744 | -34123. |

| <i>m/mol·kg⁻¹</i> | <i>σ(φ)</i> | <i>σ(lnγ)</i> | <i>σ(γ)</i> |
|------------------------------|-------------|---------------|-------------|
| .001 | .0001 | .0002 | .0001 |
| .010 | .0005 | .0012 | .0008 |
| .100 | .0018 | .0052 | .0021 |
| 1.000 | .0022 | .0063 | .0009 |
| 2.000 | .0031 | .0077 | .0007 |
| 2.400 | .0044 | .0077 | .0007 |

Coefficients of Correlating Equations

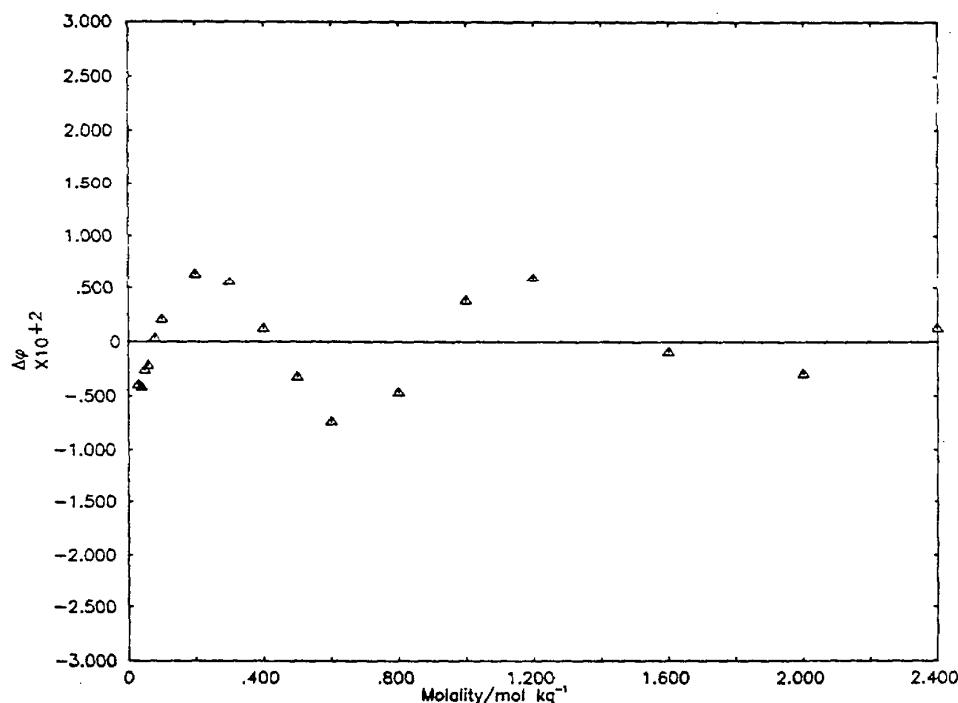
| Par | Eqs 1 | | Eqs 2 | | Eqs 3 | |
|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | coefficient | <i>σ(coeff)</i> | coefficient | <i>σ(coeff)</i> | coefficient | <i>σ(coeff)</i> |
| 1 | .9929434566+00 | .331-01 | -.5205317126+01 | .438+00 | .5986852959+01 | .172+00 |
| 2 | -.5880831391+00 | .535-01 | .2856561422+02 | .237+01 | -.8333401811+01 | .639+00 |
| 3 | .1671993808+00 | .331-01 | -.4026380543+02 | .511+01 | .7019194039+01 | .917+00 |
| 4 | -.2011584158-01 | .738-02 | .3508871349+02 | .536+01 | -.3087116233+01 | .578+00 |
| 5 | | | -.1586464626+02 | .271+00 | .5494769115+00 | .133+00 |
| 6 | | | .2866917885+01 | .529+00 | | |

$$\begin{aligned} \sigma(\text{eqs 1}) &= .458-02 \\ \sigma(\text{eqs 2}) &= .495-02 \\ \sigma(\text{eqs 3}) &= .387-02 \end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Masterton et al [21]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_c data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol kg}^{-1}$ | $\phi_{298.15}$ |
|------------------------|-----------------|
| .030000 | .8290 |
| .040000 | .8110 |
| .050000 | .7980 |
| .060000 | .7860 |
| .080000 | .7680 |
| .100000 | .7530 |
| .200000 | .7000 |
| .300000 | .6610 |
| .400000 | .6270 |
| .500000 | .5980 |
| .600000 | .5730 |
| .800000 | .5420 |
| 1.000000 | .5250 |
| 1.200000 | .5080 |
| 1.600000 | .4770 |
| 2.000000 | .4640 |
| 2.400000 | .4640 |



Deviation Plot For $\text{trans-}[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NH}_3\text{NO}_2]\text{Br}_2$: $\Delta\phi$ vs molality

▲ Masterton et al [21] - vapor pressure osmometry

trans-[Co(C₂H₈N₂)NH₃NO₂]Cl₂

Recommended Values for the mean activity and osmotic coefficient of trans-[Co(C₂H₈N₂)NH₃NO₂]Cl₂ in H₂O at 298.15 K

| <i>m/mol·kg⁻¹</i> | γ | ϕ | a_w | $\Delta G^{\text{ex}}/\text{J} \cdot \text{kg}^{-1}$ |
|------------------------------|----------|--------|---------|--|
| .001 | .8651 | .9604 | .999948 | -1. |
| .002 | .8446 | .9458 | .999898 | -2. |
| .003 | .8158 | .9352 | .999848 | -3. |
| .004 | .7930 | .9267 | .999800 | -5. |
| .005 | .7738 | .9194 | .999752 | -7. |
| .006 | .7573 | .9131 | .999704 | -9. |
| .007 | .7427 | .9074 | .999657 | -11. |
| .008 | .7295 | .9023 | .999610 | -13. |
| .009 | .7176 | .8976 | .999563 | -15. |
| .010 | .7067 | .8932 | .999517 | -18. |
| .020 | .6290 | .8615 | .999069 | -48. |
| .030 | .5798 | .8404 | .998638 | -86. |
| .040 | .5438 | .8245 | .998219 | -129. |
| .050 | .5155 | .8117 | .997809 | -176. |
| .060 | .4923 | .8009 | .997406 | -227. |
| .070 | .4727 | .7916 | .997010 | -282. |
| .080 | .4557 | .7834 | .996619 | -339. |
| .090 | .4408 | .7760 | .996232 | -398. |
| .100 | .4275 | .7693 | .995851 | -461. |
| .200 | .3426 | .7235 | .992210 | -1182. |
| .300 | .2959 | .6949 | .988796 | -2036. |
| .400 | .2646 | .6738 | .985540 | -2985. |
| .500 | .2415 | .6571 | .982399 | -4009. |
| .600 | .2235 | .6436 | .979345 | -5095. |
| .700 | .2091 | .6326 | .976352 | -6235. |
| .800 | .1972 | .6235 | .973400 | -7421. |
| .900 | .1871 | .6162 | .970473 | -8648. |
| 1.000 | .1786 | .6103 | .967553 | -9912. |
| 1.250 | .1620 | .6009 | .960215 | -13209. |
| 1.500 | .1501 | .5974 | .952722 | -16667. |
| 1.750 | .1411 | .5979 | .945021 | -20252. |
| 2.000 | .1341 | .6006 | .937138 | -23941. |
| 2.250 | .1284 | .6040 | .929179 | -27718. |
| 2.400 | .1254 | .6057 | .924437 | -30021. |

| <i>m/mol·kg⁻¹</i> | $\sigma(\phi)$ | $\sigma(\ln\gamma)$ | $\sigma(\gamma)$ |
|------------------------------|----------------|---------------------|------------------|
| .001 | .0001 | .0001 | .0001 |
| .010 | .0005 | .0011 | .0008 |
| .100 | .0016 | .0045 | .0019 |
| 1.000 | .0018 | .0054 | .0010 |
| 2.000 | .0026 | .0066 | .0009 |
| 2.400 | .0038 | .0066 | .0008 |

Coefficients of Correlating Equations

| Par | Eqs 1 | | Eqs 2 | | Eqs 3 | |
|-----|-----------------|------------------------|-----------------|------------------------|-----------------|------------------------|
| | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ | coefficient | $\sigma(\text{coeff})$ |
| 1 | .1091399364+01 | .293-01 | -.4461734423+01 | .385+00 | .6519378323+01 | .135+00 |
| 2 | -.4500087573+00 | .424-01 | .2679690338+02 | .208+01 | -.8866682905+01 | .503+00 |
| 3 | .1595421536+00 | .270-01 | -.3728105309+02 | .449+01 | .7232420854+01 | .722+00 |
| 4 | -.2230783721-01 | .611-02 | .3216931328+02 | .471+01 | -.3053021421+01 | .455+00 |
| 5 | | | -.1439312904+02 | .238+01 | .5163719665+00 | .105+00 |
| 6 | | | .2572301164+01 | .465+00 | | |

$$\sigma(\text{eqs 1}) = .389-02$$

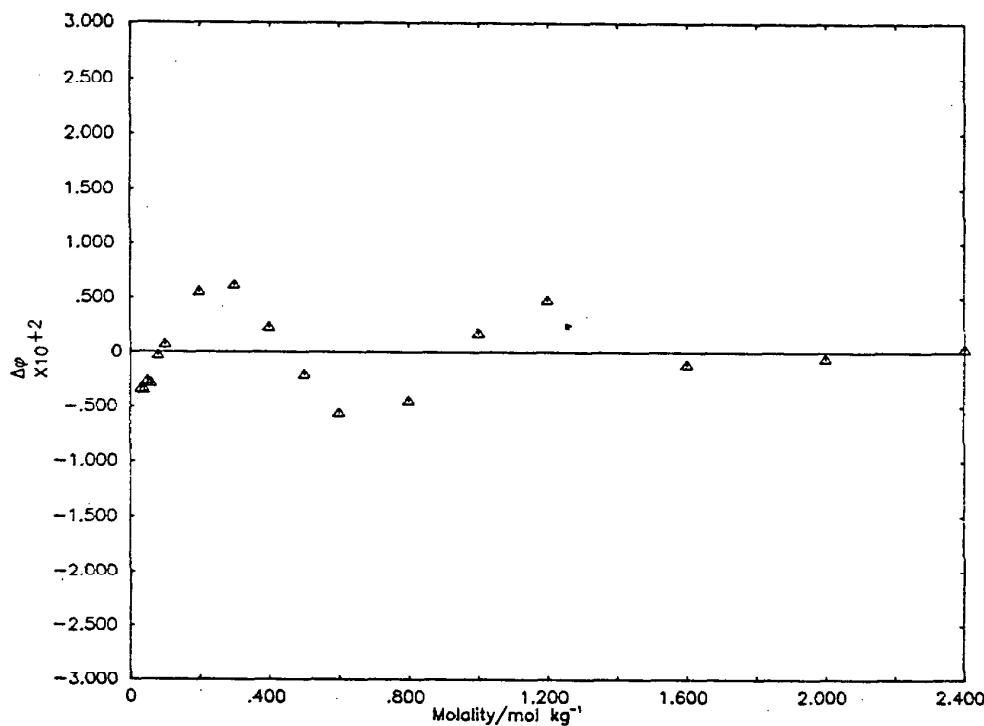
$$\sigma(\text{eqs 2}) = .435-02$$

$$\sigma(\text{eqs 3}) = .305-02$$

Experimental Data Employed in Generation of Correlating Equations

Masterton et al. [21]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_c data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\phi_{298.15}$ |
|-------------------------------------|-----------------|
| .030000 | .8370 |
| .040000 | .8210 |
| .050000 | .8090 |
| .060000 | .7980 |
| .080000 | .7830 |
| .100000 | .7700 |
| .200000 | .7290 |
| .300000 | .7010 |
| .400000 | .6760 |
| .500000 | .6550 |
| .600000 | .6380 |
| .800000 | .6190 |
| 1.000000 | .6120 |
| 1.200000 | .6070 |
| 1.600000 | .5960 |
| 2.000000 | .6000 |
| 2.400000 | .6060 |



Deviation Plot For $\text{trans}-[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NH}_3\text{NO}_2]\text{Cl}_2$: $\Delta\phi$ vs molality

▲ Masterton et al [21] - vapor pressure osmometry

cis-[Co(C₂H₈N₂)NH₃NO₂] (NO₃)₂

Recommended Values for the mean activity and osmotic coefficient of
 cis-[Co(C₂H₈N₂)NH₃NO₂] (NO₃)₂ in H₂O at 298.15 K

| <i>m/mol·kg⁻¹</i> | <i>γ</i> | <i>φ</i> | <i>a_w</i> | $ΔG^{\text{ex}}/\text{J} \cdot \text{kg}^{-1}$ |
|------------------------------|----------|----------|----------------------|--|
| .001 | .8842 | .9599 | .999948 | -1. |
| .002 | .8429 | .9448 | .999898 | -2. |
| .003 | .8134 | .9338 | .999849 | -3. |
| .004 | .7899 | .9248 | .999800 | -5. |
| .005 | .7702 | .9172 | .999752 | -7. |
| .006 | .7531 | .9105 | .999705 | -9. |
| .007 | .7380 | .9044 | .999658 | -11. |
| .008 | .7244 | .8989 | .999611 | -13. |
| .009 | .7120 | .8939 | .999565 | -16. |
| .010 | .7007 | .8892 | .999520 | -18. |
| .020 | .6195 | .8545 | .999077 | -50. |
| .030 | .5678 | .8310 | .998653 | -89. |
| .040 | .5298 | .8129 | .998244 | -133. |
| .050 | .4998 | .7981 | .997846 | -183. |
| .060 | .4752 | .7855 | .997456 | -236. |
| .070 | .4543 | .7745 | .997074 | -293. |
| .080 | .4362 | .7646 | .996699 | -354. |
| .090 | .4203 | .7557 | .996331 | -417. |
| .100 | .4061 | .7476 | .995968 | -482. |
| .200 | .3149 | .6682 | .992589 | -1255. |
| .300 | .2640 | .6464 | .989574 | -2182. |
| .400 | .2293 | .6120 | .986856 | -3227. |
| .500 | .2035 | .5824 | .984386 | -4368. |
| .600 | .1834 | .5560 | .982105 | -5591. |

| <i>m/mol·kg⁻¹</i> | $σ(φ)$ | $σ(\ln γ)$ | $σ(γ)$ |
|------------------------------|--------|------------|--------|
| .001 | .0000 | .0001 | .0001 |
| .010 | .0002 | .0004 | .0003 |
| .100 | .0003 | .0008 | .0003 |
| .600 | .0006 | .0010 | .0002 |

Coefficients of Correlating Equations

| Par | Eqs 1 | | Eqs 2 | | Eqs 3 | |
|-----|-----------------|-------------------|-----------------|-------------------|-----------------|-------------------|
| | coefficient | $σ(\text{coeff})$ | coefficient | $σ(\text{coeff})$ | coefficient | $σ(\text{coeff})$ |
| 1 | .9191110165+00 | .187-01 | -.5809298312+01 | .212+00 | .5758905962+01 | .798-01 |
| 2 | -.4209988203+00 | .634-01 | .3232462561+02 | .156+01 | -.7567906060+01 | .410+00 |
| 3 | -.2105690548+00 | .116+00 | -.4925788990+02 | .434+01 | .5525137661+01 | .709+00 |
| 4 | .2108699123+00 | .906-01 | .4232230189+02 | .528+01 | -.1679768012+01 | .402+00 |
| 5 | | | -.1461163169+02 | .236+01 | | |

$$σ(\text{eqs 1}) = .567-03$$

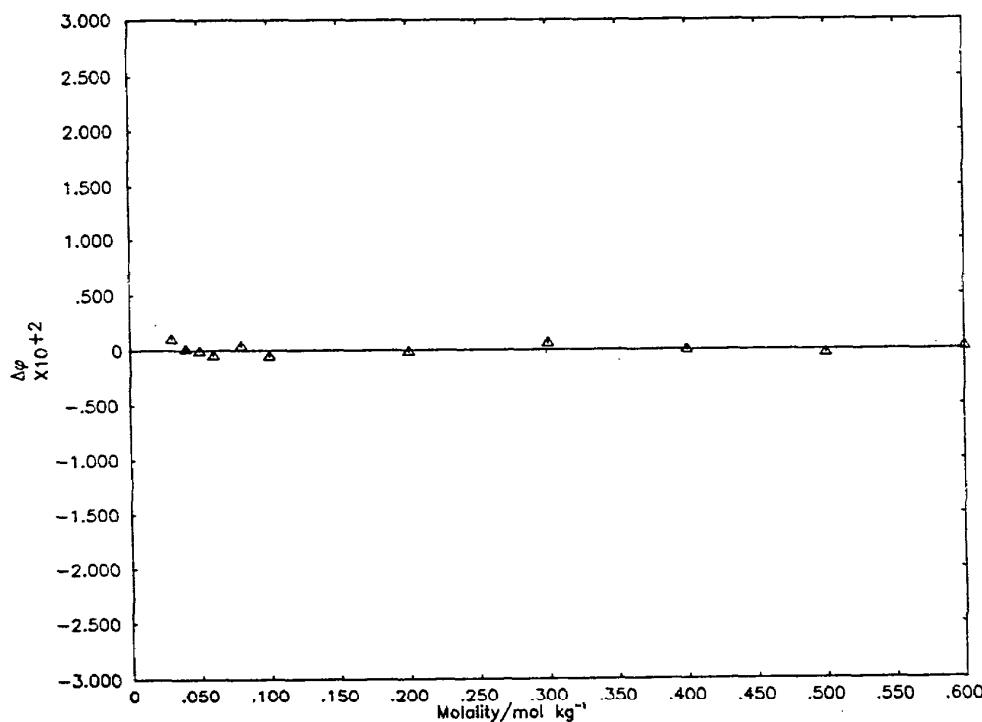
$$σ(\text{eqs 2}) = .716-03$$

$$σ(\text{eqs 3}) = .782-03$$

Experimental Data Employed in Generation of Correlating Equations

Masterton et al [21]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_c data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | ϕ |
|-------------------------------------|---------------|
| | <u>298.15</u> |
| .030000 | .8320 |
| .040000 | .8130 |
| .050000 | .7960 |
| .060000 | .7850 |
| .080000 | .7650 |
| .100000 | .7470 |
| .200000 | .6880 |
| .300000 | .6470 |
| .400000 | .6120 |
| .500000 | .5820 |
| .600000 | .5570 |



Deviation Plot For cis-[$\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NH}_3\text{NO}_2$] $_2$ (NO_3) $_2$: $\Delta\phi$ vs molality

▲ Masterton et al [21] - vapor pressure osmometry

cis-[Co(C₂H₈N₂)NH₃NO₂]I₂

Recommended Values for the mean activity and osmotic coefficient of cis-[Co(C₂H₈N₂)NH₃NO₂]I₂ in H₂O at 298.15 K

| <i>m/mol·kg⁻¹</i> | <i>y</i> | <i>θ</i> | <i>a_w</i> | $\Delta G^{\text{ex}} / \text{J} \cdot \text{kg}^{-1}$ |
|------------------------------|----------|----------|----------------------|--|
| .001 | .8839 | .9598 | .959948 | -1. |
| .002 | .8425 | .9446 | .959898 | -2. |
| .003 | .8129 | .9335 | .959849 | -3. |
| .004 | .7894 | .9245 | .959800 | -5. |
| .005 | .7696 | .9169 | .959752 | -7. |
| .006 | .7525 | .9102 | .959705 | -9. |
| .007 | .7374 | .9041 | .959658 | -11. |
| .008 | .7237 | .8987 | .959612 | -13. |
| .009 | .7114 | .8937 | .959565 | -16. |
| .010 | .7000 | .8890 | .959520 | -18. |
| .020 | .6193 | .8549 | .959076 | -50. |
| .030 | .5682 | .8321 | .952652 | -89. |
| .040 | .5308 | .8148 | .958240 | -133. |
| .050 | .5014 | .8007 | .957839 | -183. |
| .060 | .4772 | .7887 | .957446 | -236. |
| .070 | .4567 | .7782 | .957060 | -293. |
| .080 | .4389 | .7687 | .956682 | -352. |
| .090 | .4222 | .7603 | .956310 | -415. |
| .100 | .4091 | .7519 | .955944 | -480. |
| .200 | .3159 | .6664 | .952608 | -1248. |
| .300 | .2607 | .6310 | .955897 | -2179. |
| .400 | .2224 | .5858 | .987417 | -3239. |
| .500 | .1949 | .5502 | .985241 | -4408. |
| .600 | .1749 | .5259 | .983089 | -5666. |

| <i>m/mol·kg⁻¹</i> | $\sigma(\theta)$ | $\sigma(\ln y)$ | $\sigma(y)$ |
|------------------------------|------------------|-----------------|-------------|
| .001 | .0000 | .0001 | .0001 |
| .010 | .0002 | .0005 | .0004 |
| .100 | .0003 | .0007 | .0003 |
| .600 | .0005 | .0009 | .0002 |

Coefficients of Correlating Equations

Eqs. 1

| Par | coefficient | $\sigma(\text{coeff})$ |
|-----|-----------------|------------------------|
| 1 | .7177177567+00 | .394-01 |
| 2 | .6103399302+00 | .176+00 |
| 3 | -.3429135930+01 | .438+00 |
| 4 | .4659847619+01 | .720+00 |
| 5 | -.2114807049+01 | .469+00 |

Eqs. 2

| coefficient | $\sigma(\text{coeff})$ |
|----------------|------------------------|
| .6642253502+01 | .295+00 |
| .3984406819+02 | .216+01 |
| .7088013482+02 | .601+01 |
| .6675957812+02 | .732+01 |
| .2421750363+02 | .327+01 |

Eqs. 3

| coefficient | $\sigma(\text{coeff})$ |
|-----------------|------------------------|
| .5738553632+01 | .568-01 |
| -.6220063257+01 | .291+00 |
| .1378908994+01 | .504+00 |
| .1306594809+01 | .286+00 |

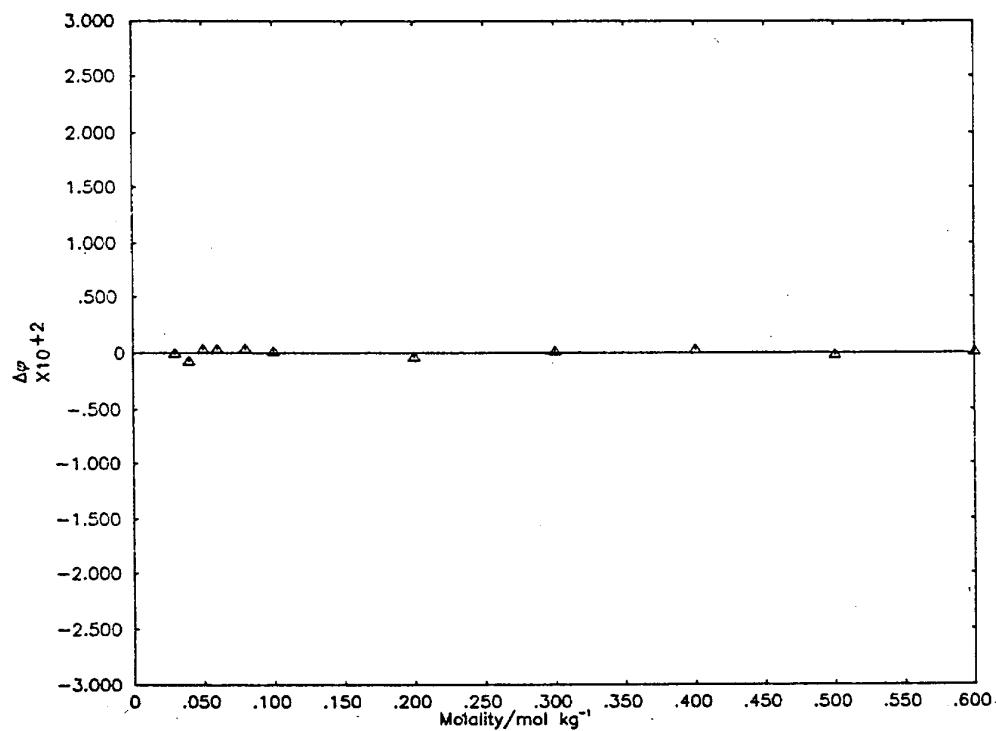
$$\begin{aligned}\sigma(\text{eqs. 1}) &= .453-03 \\ \sigma(\text{eqs. 2}) &= .933-03 \\ \sigma(\text{eqs. 3}) &= .556-03\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equation

Masterton et al [21]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_c data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

$$\frac{m}{\text{mol} \cdot \text{kg}^{-1}} \quad \phi_{298.15}$$

| | |
|----------|--------|
| • 030000 | • 8320 |
| • 040000 | • 8140 |
| • 050000 | • 8010 |
| • 060000 | • 7890 |
| • 080000 | • 7690 |
| • 100000 | • 7520 |
| • 200000 | • 6860 |
| • 300000 | • 6320 |
| • 400000 | • 5860 |
| • 500000 | • 5500 |
| • 600000 | • 5260 |



Deviation Plot For $\text{cis}-[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NH}_3\text{NO}_2]\text{I}_2$: $\Delta\phi$ vs molality

▲ Masterton et al [21] - vapor pressure osmometry

cis[Co(C₂H₈N₂)NH₃NO₂]Br₂

Recommended Values for the mean activity and osmotic coefficient of cis-[Co(C₂H₈N₂)NH₃NO₂]Br₂ in H₂O at 298.15 K

| <i>m/mol·kg⁻¹</i> | <i>γ</i> | <i>φ</i> | <i>a_w</i> | <i>ΔG^{ex/J·kg⁻¹}</i> |
|------------------------------|----------|----------|----------------------|--|
| .001 | .8838 | .9597 | .999948 | -1. |
| .002 | .8421 | .9444 | .999898 | -2. |
| .003 | .8124 | .9332 | .999849 | -3. |
| .004 | .7886 | .9240 | .999800 | -5. |
| .005 | .7627 | .9162 | .999752 | -7. |
| .006 | .7514 | .9094 | .999705 | -9. |
| .007 | .7361 | .9032 | .999658 | -11. |
| .008 | .7223 | .8976 | .999612 | -13. |
| .009 | .7097 | .8924 | .999566 | -16. |
| .010 | .6962 | .8876 | .999520 | -18. |
| .020 | .6156 | .8517 | .999080 | -50. |
| .030 | .5630 | .8273 | .998660 | -90. |
| .040 | .5243 | .8084 | .998264 | -136. |
| .050 | .4938 | .7930 | .997859 | -185. |
| .060 | .4627 | .7798 | .997474 | -240. |
| .070 | .4475 | .7683 | .997098 | -298. |
| .080 | .4291 | .7580 | .996728 | -359. |
| .090 | .4130 | .7488 | .996365 | -424. |
| .100 | .3986 | .7403 | .996007 | -491. |
| .200 | .3067 | .6789 | .992689 | -1280. |
| .300 | .2559 | .6363 | .989735 | -2229. |
| .400 | .2215 | .6015 | .987080 | -3298. |
| .500 | .1960 | .5715 | .984676 | -4466. |
| .600 | .1762 | .5455 | .982467 | -5718. |
| .700 | .1605 | .5236 | .980385 | -7045. |
| .800 | .1478 | .5064 | .978342 | -8437. |
| .900 | .1377 | .4945 | .976231 | -9885. |
| 1.000 | .1298 | .4888 | .973927 | -11382. |

| <i>m/mol·kg⁻¹</i> | <i>σ(φ)</i> | <i>σ(lnγ)</i> | <i>σ(γ)</i> |
|------------------------------|-------------|---------------|-------------|
| .001 | .0000 | .0001 | .0001 |
| .010 | .0003 | .0007 | .0005 |
| .100 | .0007 | .0022 | .0009 |
| 1.000 | .0016 | .0028 | .0004 |

Coefficients of Correlating Equations

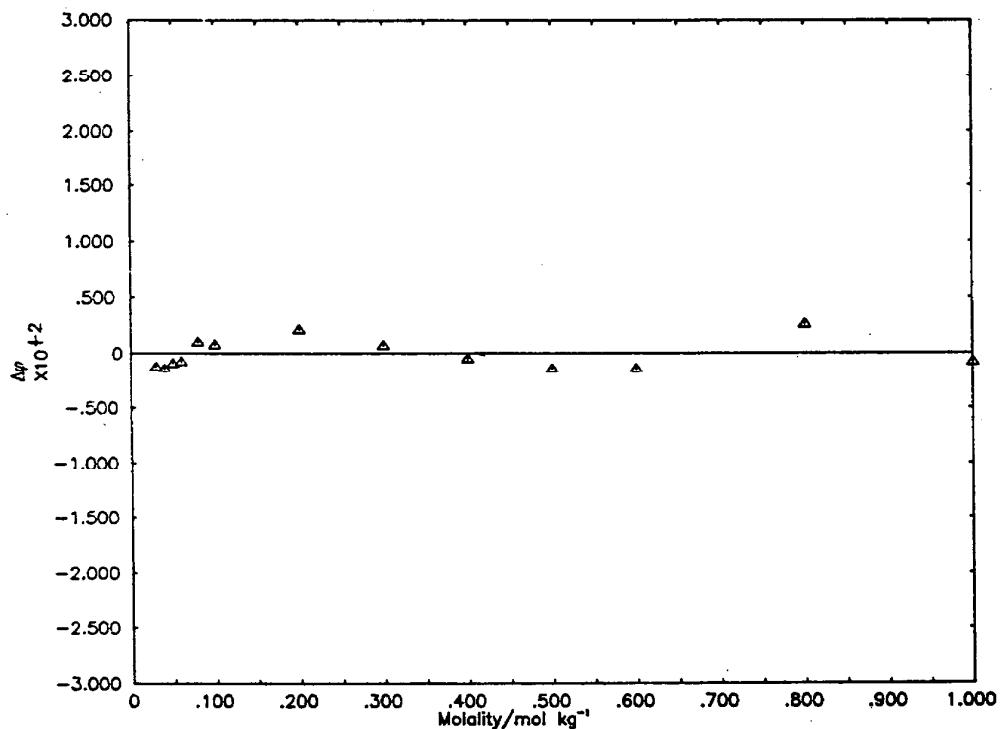
| | <u>Eqs 1</u> | <u>Eqs 2</u> | <u>Eqs 3</u> |
|-----|--------------------|-----------------|--------------------|
| Par | <u>coefficient</u> | <u>σ(coeff)</u> | <u>coefficient</u> |
| 1 | .8350063743+00 | .265-01 | -.6085415820+01 |
| 2 | -.3308338378+00 | .797-01 | .3164835313+02 |
| 3 | -.2721356446+00 | .966-01 | -.4390216662+02 |
| 4 | .2269103881+00 | .476-01 | .3334285107+02 |
| 5 | | | -.9915690944+01 |
| | | | .103+01 |

$$\begin{aligned} \sigma(\text{eqs 1}) &= .162-02 \\ \sigma(\text{eqs 2}) &= .171-02 \\ \sigma(\text{eqs 3}) &= .100-02 \end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Masterton et al [21]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_c data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol} \cdot \text{kg}^{-1}$ | $\phi_{298.15}$ |
|-------------------------------------|-----------------|
| .030000 | .8260 |
| .040000 | .8070 |
| .050000 | .7920 |
| .060000 | .7790 |
| .080000 | .7590 |
| .100000 | .7410 |
| .200000 | .6810 |
| .300000 | .6370 |
| .400000 | .6010 |
| .500000 | .5700 |
| .600000 | .5440 |
| .800000 | .5090 |
| 1.000000 | .4880 |



Deviation Plot For cis-[$\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NH}_3\text{NO}_2$]Br₂: $\Delta\phi$ vs molality

▲ Masterton et al [21] - vapor pressure osmometry

cis-[Co(C₂H₈N₂)NH₃NO₂]Cl₂

Recommended Values for the mean activity and osmotic coefficient of cis-[Co(C₂H₈N₂)NH₃NO₂]Cl₂ in H₂O at 298.15 K

| <i>m/mol·kg</i> ⁻¹ | <i>Y</i> | <i>φ</i> | <i>a_w</i> | $\Delta G^{\text{ex}}/\text{J} \cdot \text{kg}^{-1}$ |
|-------------------------------|----------|----------|----------------------|--|
| .001 | .8850 | .9604 | .999948 | -1. |
| .002 | .8444 | .9457 | .999898 | -2. |
| .003 | .8156 | .9351 | .999848 | -3. |
| .004 | .7927 | .9265 | .999800 | -5. |
| .005 | .7735 | .9192 | .999752 | -7. |
| .006 | .7565 | .9128 | .999704 | -9. |
| .007 | .7422 | .9071 | .999657 | -11. |
| .008 | .7291 | .9019 | .999610 | -13. |
| .009 | .7171 | .8972 | .999564 | -15. |
| .010 | .7061 | .8928 | .999518 | -18. |
| .020 | .6280 | .8607 | .999070 | -48. |
| .030 | .5784 | .8293 | .998640 | -86. |
| .040 | .5421 | .8230 | .998222 | -129. |
| .050 | .5135 | .8098 | .997814 | -177. |
| .060 | .4900 | .7966 | .997414 | -228. |
| .070 | .4701 | .7889 | .997020 | -283. |
| .080 | .4529 | .7803 | .996632 | -341. |
| .090 | .4377 | .7726 | .996249 | -401. |
| .100 | .4242 | .7656 | .995871 | -463. |
| .200 | .3375 | .7162 | .992289 | -1193. |
| .300 | .2894 | .6841 | .988970 | -2061. |
| .400 | .2570 | .6595 | .985844 | -3029. |
| .500 | .2329 | .6355 | .982867 | -4077. |
| .600 | .2142 | .6227 | .980008 | -5103. |
| .700 | .1990 | .6085 | .977242 | -6367. |
| .800 | .1864 | .5963 | .974545 | -7592. |
| .900 | .1758 | .5860 | .971898 | -8863. |
| 1.000 | .1668 | .5773 | .969283 | -10176. |
| 1.250 | .1491 | .5613 | .962788 | -13614. |
| 1.500 | .1363 | .5522 | .956218 | -17239. |
| 1.750 | .1266 | .5483 | .949461 | -21015. |
| 2.000 | .1192 | .5481 | .942480 | -24915. |
| 2.250 | .1132 | .5500 | .935305 | -28919. |
| 2.500 | .1083 | .5528 | .928035 | -33011. |
| 2.750 | .1040 | .5549 | .920834 | -37181. |
| 2.800 | .1032 | .5552 | .919421 | -38024. |

| <i>m/mol·kg</i> ⁻¹ | $\sigma(\phi)$ | $\sigma(\ln y)$ | $\sigma(Y)$ |
|-------------------------------|----------------|-----------------|-------------|
| .001 | .0001 | .0002 | .0002 |
| .010 | .0006 | .0014 | .0010 |
| .100 | .0021 | .0059 | .0025 |
| 1.000 | .0024 | .0073 | .0012 |
| 2.000 | .0033 | .0085 | .0010 |
| 2.800 | .0049 | .0087 | .0009 |

Coefficients of Correlating Equations

Eqs. 1

| Par | coefficient | $\sigma(\text{coeff})$ |
|-----|-----------------|------------------------|
| 1 | .1088759074+01 | .358-01 |
| 2 | -.5196348468+00 | .467-01 |
| 3 | .1602028661+00 | .256-01 |
| 4 | -.1964073261-01 | .495-02 |
| 5 | | |
| 6 | | |

Eqs. 2

| coefficient | $\sigma(\text{coeff})$ |
|-----------------|------------------------|
| -.4050015680+01 | .394+00 |
| .2391831812+02 | .190+01 |
| -.3060292713+02 | .373+01 |
| .2471654150+02 | .357+01 |
| -.1039164063+02 | .166+01 |
| .1745752336+01 | .299+00 |

Eqs. 3

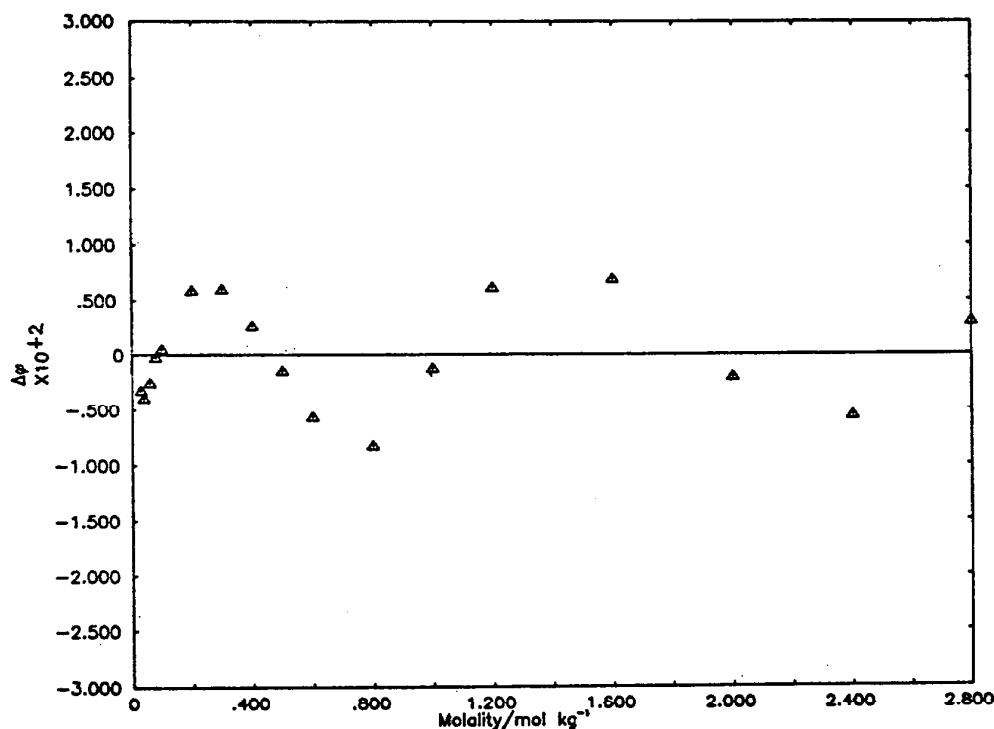
| coefficient | $\sigma(\text{coeff})$ |
|-----------------|------------------------|
| .6568763321+01 | .143+00 |
| -.9303571606+01 | .486+00 |
| .7790660050+01 | .639+00 |
| -.3346305727+01 | .369+00 |
| .5725151722+00 | .783-01 |

$$\begin{aligned}\sigma(\text{eqs. 1}) &= .514-02 \\ \sigma(\text{eqs. 2}) &= .519-02 \\ \sigma(\text{eqs. 3}) &= .353-02\end{aligned}$$

Experimental Data Employed in Generation of Correlating Equations

Masterton et al [21]. Vapor pressure osmometry measurements performed at 37°C. ϕ_L and ϕ_c data for CoCl_2 were used to adjust this data to 25°C. Assigned weight is 1.0.

| $m/\text{mol kg}^{-1}$ | $\phi_{298.15}$ |
|------------------------|-----------------|
| .030000 | .8360 |
| .040000 | .8190 |
| .060000 | .7960 |
| .080000 | .7800 |
| .100000 | .7660 |
| .200000 | .7220 |
| .300000 | .6900 |
| .400000 | .6620 |
| .500000 | .6380 |
| .600000 | .6170 |
| .800000 | .5880 |
| 1.000000 | .5760 |
| 1.200000 | .5700 |
| 1.600000 | .5570 |
| 2.000000 | .5460 |
| 2.400000 | .5460 |
| 2.800000 | .5580 |



Deviation Plot For $\text{cis}-[\text{Co}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NH}_3\text{NO}_2]\text{Cl}_2$: $\Delta\phi$ vs molality

Δ Masterton et al [21] - vapor pressure osmometry

3.5. Systems Not Treated

King et al. [14] have reported freezing point depression measurements for aqueous solutions of $[Ni(NH_3)_6](NO_3)_2$ and $[Ni(C_6H_5N)_6](NO_3)_2$. The measurements are not very precise and do not appear to be very accurate since only a crude Beckmann type apparatus was used. Hence we have not treated the data for these systems.

3.6. Comparison with Previous Compilations and Evaluations

Earlier 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 [15] and Robinson and Stokes [16], and in the papers of Wu and Hamer [17] and Pitzer and Mayorga [18]. It should be noted that evaluated data for $Co(ClO_4)_2$, $Ni(ClO_4)_2$, and all of the cobalt complex compounds dealt with herein, with the exception of *cis*- and *trans*- $[Co(C_2H_8N_2)_2NH_2NO_2]X_2$, where $X = NO_3, I, Br, or Cl$, have not appeared in any of these earlier sources.

The tables given by Robinson and Stokes [16] appear to be exclusively based upon their own isopiestic measurements and Harned and Owen [15] also based their tables, which are not as extensive as those given by Robinson and Stokes [16], upon earlier calculations performed by Robinson and Stokes [19] and also based on these same isopiestic measurements. Comparison of the activity coefficients at the maximum molalities given in the tables of Robinson and Stokes [16] with our own values show an average difference of 1.8%, which appears to be random, and a maximum difference of 2.7%; this maximum difference is for $CoCl_2$ where we have included the recent experimental data of Downes [20].

Wu and Hamer [17] and Pitzer and Mayorga [18], like ourselves, have made use of modern digital computers which were not available to either Robinson and Stokes [16] or to Harned and Owen [15]. Wu and Hamer [17] used an equation that differs from our equation (1a) only in that it gives $\log_{10} \gamma$ rather than $\ln \gamma$. While the equations of Pitzer and Mayorga [18] differ from those we have used, they still include the Debye-Hückel limiting law, and insofar as the parameters they calculate are based on experimental data, their results remain essentially empirical in nature. The coefficients given by Pitzer and Mayorga [18] are based upon either the smoothed osmotic coefficients given by Robinson and Stokes [16] or, for *cis*- and

trans- $[Co(C_2H_8N_2)NH_2NO_2]X_2$, where $X = NO_3, I, Br, or Cl$, upon the reported osmotic coefficients of Masterton et al. [21]. Pitzer and Mayorga [18], gave additional physical interpretation to their calculated parameters but did not give fits out to the maximum molalities for which experimental data existed for several systems. Wu and Hamer [17], while citing additional sources of data for several of the systems, do not state how these various data sets were weighted and for two systems ($NiCl_2$ and $CoBr_2$) their tables give values for the activity and osmotic coefficients at molalities greater than that for which there is experimental data. Comparison of our calculated activity coefficients with those of Pitzer and Mayorga [18] and Wu and Hamer [17] at the maximum possible molalities show an average difference of 4 and 3 percent, and a maximum difference of 10 and 7 percent, respectively. The maximum difference with the calculations of Pitzer and Mayorga [18] occurs for *cis*- $[Co(C_2H_8N_2)NH_2NO_2]Cl_2$ and is equal to 0.011 for an activity coefficient equal to 0.103 at 2.4 mol $\cdot kg^{-1}$; this difference may be attributable to either the different correlating equations we have used or to the adjustment of the osmotic coefficient data of Masterton et al. [21] from 37 to 25 °C. The maximum difference with the calculations of Wu and Hamer [17] occurs for $FeCl_2$ and is equal to 0.056 for an activity coefficient equal to 0.776 at 2.0 mol $\cdot kg^{-1}$; it may be attributable to differences in the way the various data sets were weighted.

4. 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], $NaClO_4$ [1], H_2SO_4 [4], $CaCl_2$ [3], NH_4Cl [1], and $CaBr_2$ [3]. For $Mg(ClO_4)_2$, 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 of the isopiestic data of Stokes and Levien [21a] and the freezing point depression data of Nicholson and Felsing [21b].

Relative Apparent Molal Enthalpy Data

The coefficients for the equation $\Phi_L/J \cdot mol^{-1} = \sum_{i=1}^N \alpha_i m^{i/2}$ were obtained by least squares fits to enthalpies of dilution calculated from the compiled values of enthalpies of formation at various molalities as given in NBS Technical Note 270-4 [22]. They are given in table I.

TABLE I. 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 |
|----------|---|------------|------------|------------|------------|------------|------------|------------|
| $FeCl_2$ | 0.056 to 2.22 | 647.093 | 61004.0 | -183886.0 | 243739.0 | -162026.0 | 53250.0 | -6867.75 |
| $NiCl_2$ | 0 to 2.78 | 10263.4 | -11231.10 | 15465.7 | -13503.4 | 6600.57 | -1215.48 | |
| $CoCl_2$ | 0 to 3.70 | 10263.4 | 13829.8 | -161829.0 | 44613.0 | -478966.0 | 175850.0 | |

Apparent Molal Heat Capacity Data

For CoCl_2 and NiCl_2 we have used, depending upon molality range of interest, two different sets of coefficients in the equation $\Phi_C / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = \Phi_C^\circ + \sum_{i=1}^N \beta_i m^{i/2}$. These 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 |
|-----------------|--|----------------|-----------|-----------|-----------|
| CoCl_2 | 0.05 to 0.24 | -278.7 | 150.38 | -61.7 | [23] |
| CoCl_2 | 0.10 to 4.2 | -280.1 | 46.38 | -20.18 | [24] |
| NiCl_2 | 0.04 to 0.20 | -294.0 | 150.38 | -67.9 | [23] |
| NiCl_2 | 0.35 to 2.04 | -266.9 | 89.96 | 0.0 | [25] |

All of the above coefficients are those given by the respective workers, except for the coefficients of CoCl_2 for the molality range 0.10 to 4.2 mol·kg⁻¹ which was obtained by a least squares fit to the experimental data.

Additional Auxiliary Data Follow:

$$\begin{aligned}\Delta H^\circ_{\text{fus}} &= 6008 \text{ J} \cdot \text{mol}^{-1} & [26] \\ \Delta C^\circ_{\text{fus}} &= 38.1 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1} & [26] \\ \Delta b &= -0.197 \text{ J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1} & [26] \\ T_{\text{fus}} &= 273.15 \text{ K for water} & [7] \\ R &= 8.31441 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} & [27] \\ F &= 96484.56 \text{ C} \cdot \text{mol}^{-1} & [27] \\ A &= 1.17625 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2} & [2] \\ P^\circ &= 3168.6 \text{ Pa (23.7627 torr)} \\ &\quad \text{for water at } 25^\circ\text{C} & [28] \\ B_T &= -992 \text{ cm}^3 \cdot \text{mol}^{-1} \text{ at } 25^\circ\text{C} & [29]\end{aligned}$$

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6. References

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| [46] Hall, R. E., and Harkins, W. D., J. Am. Chem. Soc. 38 , 2658 (1916). | T | thermodynamic or absolute temperature |
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| [48] Robinson, R. A., Trans. Faraday Soc. 34 , 1142 (1938). | α_i | coefficients in a specified equation |
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| [50b] Libus, Z., personal communication. | μ | chemical potential |
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| [52] Robinson, R. A., Wilson, J. M., and Ayling, H. S., J. Am. Chem. Soc. 64 , 1469 (1942). | v | total number of ions formed from one molecule of solute assuming complete dissociation: [$v = \sum_i v_i$] |
| | ρ_B or ρ | mass concentration or density of a given system |
| | ρ° | mass concentration or density of pure solvent |
| | σ | standard deviation |
| | ϕ or φ | osmotic coefficient |
| | Φ_C | apparent molal heat capacity |
| | Φ_L | relative apparent molal enthalpy |

7. Glossary and Symbols

| | |
|--------------|--|
| a_w | activity of water |
| Δb | $(\partial \Delta C_s / \partial T)_p$ |
| c_B or c | concentration of solute substance B |
| m_B or m | molality of solute substance B |
| x_B or x | mole fraction of substance B |
| z_B | charge number of an ion B |
| A | constant in Debye-Hückel limiting law |
| A_1 | $ z_+ z_- A$ |
| A_2 | $\frac{(\sum_i v_i z_i^3)^2}{3v \sum_i (v_i z_i^2)} A^2$ |
| | v |
| | total number of ions formed from one molecule of solute assuming complete dissociation: [$v = \sum_i v_i$] |
| | ρ_B or ρ |
| | mass concentration or density of a given system |
| | ρ° |
| | mass concentration or density of pure solvent |
| | σ |
| | standard deviation |
| | ϕ or φ |
| | osmotic coefficient |
| | Φ_C |
| | apparent molal heat capacity |
| | Φ_L |
| | relative apparent molal enthalpy |