Activity and Osmotic Coefficients of Aqueous Alkali Metal Nitrites

Bert R. Staples

Electrolyte Data Center, Chemical Thermodynamics Division, Center for Thermodynamics and Molecular Science, National Bureau of Standards, Washington, DC 20234

A critical evaluation of the mean activity $\gamma_{\pm}$, and osmotic coefficients, ϕ, of aqueous alkali metal nitrites at 298.15 K is presented for the molality range from dilute to saturation. Osmotic coefficients were calculated from static vapor pressure measurements. A non-linear least-squares program was used to fit ϕ data as a function of molality. Several equations describe the osmotic coefficient, the mean activity coefficient, and the excess Gibbs energy as a function of the square-root of molality for each salt. The scientific literature was covered through March 1979.

Key words: Activity coefficients; alkali metal nitrite salts; aqueous; critical evaluation; $CsNO_2$; electrolytes; excess Gibbs energy; KNO_2, $LiNO_2$, $NaNO_2$; osmotic coefficients; $RbNO_2$; solutions, standard reference data; thermodynamic properties.

1. Introduction

This correlation presents values for the activity and osmotic coefficients and the activity of water at saturation for the nitrites of lithium, sodium, potassium, rubidium, and cesium. These data were required by the Chemical Thermodynamics Data Center at the National Bureau of Standards to calculate the Gibbs energy of solution for the nitrites from several sources of experimental data.

No compilation or critical evaluation of activity data for the alkali metal nitrites has been published. These salts are not included in recent compilations of activity and osmotic coefficients by Hamer and Wu [1][1] or in standard texts, such as Robinson and Stokes [2], Harned and Owen [3], and Pitzer and Brewer [4]. By means of a correlation of all existing activity data on these electrolytes, the Electrolyte Data Center presents these values for the activity of water and the mean activity coefficient of the alkali metal nitrites at saturation.

2. Procedures

Detailed discussions of the procedures used in this evaluation may be found in previously published works (Staples and Nuttall [5,6], and Staples, [7]).

Sources of data included files of the Chemical Thermodynamics Data Center (NBS), the Electrolyte Data Center and a computer search of a commercial data base containing Chemical Abstracts, Chemical Condensates, and the National Technical Information System files. The extensive bibliography on activity data, compiled by Goldberg, Staples, Nuttall, and Arbuckle was used as the main source of data. Literature considered extends through March 1979.

In the literature search of the properties of the alkali nitrites, static vapor pressure measurement was the only experimental method which provided data for activity calculations. From these vapor pressure measurements, the osmotic coefficient, ϕ, and the activity of the solvent, a_1, were determined as follows:

$$\ln a_1 = \ln(P/P_0) + \frac{B_T(P - P_0)}{RT}, \tag{1}$$

and

$$\phi = -\frac{1000}{\nu m M_1} \ln a_1. \tag{2}$$

where M_1 is the molecular weight of solvent ($M_{H_2O} = 18.0154$ g·mol^{-1}), ν is the number of ions, m the molality (moles of solute per kilogram of water), P is the partial pressure of the water vapor over the solution, P_0 is that over pure water, and R is the gas constant, 8.31441 J·mol^{-1}·K^{-1}. At $T = 298.15$ K we take $P_0 = 3168.6$ Pa (23.7665 Torr) [9], and the second virial coefficient for water, $B_T = -992$ cm^3·mol^{-1} from the Steam Tables [10]. Corrections for the non-ideality of water vapor are given by the second term on the right of eq (1), these corrections are, at most, about 0.1% of ϕ.

For each salt, activities were correlated by means of a non-linear least squares procedure (Staples and Nuttall [5,6]). The data were accurately described by modified Hamer-Wu [1] equations

$$\ln \gamma = \frac{-|z_+z_-|AI^{1/2}}{1 + BI^{1/2}} + Cm + Dm^2 + Em^3 + \ldots \tag{3}$$

$$\phi = 1 + \frac{|z_+z_-|A}{B^3 I}[-(1 + BI^{1/2}) + 2\ln(1 + BI^{1/2}) + 1/(1 + BI^{1/2}] + (1/2)Cm + (2/3)Dm^2 + (3/4)Em^3 + \ldots, \tag{4}$$

and

$$\Delta G^{ex} = \nu m R T \frac{|z_+z_-|A}{B^3 I} \times [(2 - BI^{1/2})BI^{1/2} - 2\ln(1 + BI^{1/2})] + (1/2)Cm + (1/3)Dm^2 + (1/4)Em^3 + \ldots, \tag{5}$$

where I is the ionic strength and equal to the molality for these nitrites. Parameters are tabulated for the correlating equations. The value, $A = 1.17625$ kg$^{1/2}$ mol$^{-1/2}$ was used [5], and $|z_+z_-| = 1$ for all these electrolytes.

[1] Figures in brackets indicate literature references.

3. Sources of Data

A literature search [8] updated to March 1978, produced few references to activity measurements of the alkali metal nitrites. All data found were reported only at the temperature of 298.15 K.

Static vapor pressure measurements for $LiNO_2$ solutions were reported by Chekhunova, Protsenko, and Venerovskaya [11] at 25 molalities from 0.1 to 19.90 mol·kg^{-1} and by Ray and Ogg [12] for 14 molalities, 0.3 to 20.5 mol·kg^{-1}. The values calculated from the original experimental data are presented in tables 1 and 2, respectively.

Chekhunova *et al.* [11] also measured vapor pressures of $RbNO_2$ from 0.3 to 62.3 mol·kg^{-1} (saturation) at 28 molalities and also at 23 molalities of $CsNO_2$ (0.1 to 36.0 mol·kg^{-1} (sat.)). The calculated results are shown in tables 7 and 8, respectively.

Ray and Ogg [12] measured vapor pressures of 7 solutions of $NaNO_2$, 0.3 to 12.34 mol·kg^{-1} and Chekhunova and Protsenko [13], 16 solutions, 0.1 to 12.25 mol·kg^{-1}. The results of my calculations based on these data are listed in tables 3 and 4, respectively.

Each of these same authors report vapor pressures for KNO_2 solutions, 0.2 to 31.18 mol·kg^{-1} (Ray and Ogg [12], 9 measurements) and 0.1 to 34.12 mol·kg^{-1} (Chekhunova and Protsenko [13], 17 measurements). The calculated results appear in tables 5 and 6.

Data published by Ray and Ogg and Chekhunova, report the highest molality as saturated. Even though these authors find slightly different molalities for saturation, all the data were included in the correlations. Values for saturation were selected from a combination of values given by these authors and the values tabulated by Linke [14]. For $LiNO_2$, saturation was reported [14] at a molality of 19.58. The average of 3 values [11, 12, 14] is 19.9, the molality given by Chekhunova *et al.* [11].

4. Correlation of Results

Equations selected for correlating the data should apply over the entire range of measurements. Not only should they reproduce the data well, but they should take into account the very dilute region where they are used to evaluate the integral resulting from the Gibbs-Duhem equation and the definitions of the activity and the osmotic coefficient (Staples and Nuttall [5]). The Gibbs-Duhem equation provides a relationship between activity coefficients which are a measure of solute activity, and osmotic coefficients which are a measure of solvent activity.

The equations which best describe the data for the alkali metal nitrites over the range of molalities from dilute to saturated are eqs (3–5) and the parameters and their standard deviations are presented in table 9 for each salt. Values for the parameters of the correlating equations were determined by a non-linear least squares fit of experimental data using eq. (4) for vapor pressure measurements that yielded solvent activity. A set of parameters for eqs (3–5) was calculated by this method which minimizes $\Sigma\, w_i [f_{\text{exptl}} - f_{\text{calc}}]^2$ where the function, $f_{\text{exptl}} = \phi$, and f_{calc} was obtained from eq (4). The weight assigned is w_i. The summation extends over all experimental points.

Initially all the experimental data were weighted equally and included in the fitting procedure. Data were then weighted zero when deviations in $f(\phi$ or $\ln \gamma)$ were beyond a reasonable value, generally 0.02 (usually more than three times the standard deviation of the fit) or about 2 percent of the calculated value of ϕ or $\ln \gamma$. Sometimes it was necessary to weight individual points zero and such points are marked with an asterisk in the data tables. All other data were weighted one.

The saturated solution of $NaNO_2$ was taken at the molality of 12.34 [13], which agreed with 12.31 [14] and 12.25 [12] mol·kg^{-1}. The molality reported for KNO_2 by Ray and Ogg [12], 34.3 mol·kg^{-1}, was in agreement with others 34.12 [13] and 36 mol·kg^{-1} [14]. The highest value appeared to be uncertain and was not selected. No other solubility data were found for $RbNO_2$ or $CsNO_2$, so the values reported by Chekhunova *et al.* [11] were used. Thus the saturation molalities selected were $LiNO_2$, 19.9; $NaNO_2$, 12.34; KNO_2, 34.12; $RbNO_2$, 62.3; and $CsNO_2$, 36.0 mol·kg^{-1}.

Tables 10–14 present recommended values for ϕ, γ, a_w and ΔG^{ex} at rounded molalities up to saturation. The equations (3–5) and the coefficients listed in table 9 are recommended for calculating the activity or osmotic coefficients for these salts over the concentration range from about 0.1 mol·kg^{-1} to saturation. Since there were no data available below 0.1 mol·kg^{-1} the values for ϕ and $\gamma_{\pm}$ calculated from these equations for lower molalities should be used with caution. However, judging from the general behavior of electrolytes in the dilute region, the ϕ and $\gamma_{\pm}$ values given below 0.1 mol·kg^{-1} appear to be reasonable.

Table 1. $LiNO_2$ Chekhunova, Protsenko, & Venerovskaya [11]

m (mol/kg)	a(w)	ø	a(w) (no correction for non-ideality)	ø
0.1000	0.99660	0.9440	0.99660	0.9452
0.3000	0.98991	0.9380	0.98990	0.9391
0.5000	0.98272	0.9675	0.98270	0.9687
0.7000	0.97553	0.9823	0.97550	0.9835
0.9000	0.96844	0.9890	0.96840	0.9902
1.0000	0.96504	0.9876	0.96500	0.9888
2.0000	0.92509	1.0806	0.92500	1.0819
3.0000	0.88183	1.1634	0.88170	1.1648
4.0000	0.83597	1.2431	0.83580	1.2445
5.0000	0.79011	1.3077	0.78990	1.3092
6.0000	0.74424	1.3650	0.74100	1.3066
7.0000	0.69547	1.4399	0.69520	1.4414
8.0000	0.64999	1.4946	0.64970	1.4961
9.0000	0.60480	1.5507	0.60450	1.5522
10.0000	0.56661	1.5767	0.56630	1.5782
11.0000	0.52912	1.6061	0.52880	1.6076
12.0000	0.49422	1.6300	0.49390	1.6315
13.0000	0.46182	1.6494	0.46150	1.6509
14.0000	0.43191	1.6643	0.43160	1.6657
15.0000	0.40531	1.6710	0.40500	1.6724
16.0000	0.38090	1.6743	0.38060	1.6757
17.0000	0.35859	1.6743	0.35830	1.6757
18.0000	0.33878	1.6689	0.33850	1.6702
19.0000	0.32028	1.6632	0.32000	1.6644
19.9000	0.30507	1.6558	0.30480	1.6570

Table 2. $LiNO_2$ Ray & Ogg [12]

m (mol/kg)	a(w)	Ø	a(w) (no correction for non-ideality)	Ø (no correction for non-ideality)
0.3315*	0.98981	0.8573	0.98980	0.8584
0.4320*	0.98622	0.8916	0.98620	0.8928
1.1330*	0.96085	0.9784	0.96080	0.9796
1.3430*	0.95186	1.0196	0.95180	1.0209
2.7400*	0.89712	1.0997	0.89700	1.1010
4.7600*	0.80920	1.2344	0.80900	1.2358
5.7900*	0.76323	1.2952	0.76300	1.2966
7.5300*	0.68827	1.3769	0.68800	1.3784
8.7600*	0.63829	1.4224	0.63800	1.4239
12.7800*	0.49732	1.5170	0.49700	1.5184
15.1000*	0.43231	1.5414	0.43200	1.5427
17.8200*	0.36930	1.5515	0.36900	1.5527
19.7700*	0.33128	1.5510	0.33100	1.5521
20.5000*	0.31727	1.5542	0.31700	1.5554

* Assigned a weight of zero in the correlation.

Table 3. $NaNO_2$ Ray & Ogg [12]

m (mol/kg)	a(w)	Ø	a(w) (no correction for non-ideality)	Ø (no correction for non-ideality)
0.3082 *	0.99031	0.8767	0.99030	0.8778
0.4320 *	0.98582	0.9177	0.98580	0.9188
0.6510	0.97923	0.8950	0.97920	0.8961
1.4180	0.95446	0.9124	0.95440	0.9135
2.9550	0.90521	0.9354	0.90510	0.9365
6.8000	0.78671	0.9791	0.78650	0.9802
12.3400	0.64289	0.9936	0.64260	0.9946

* Assigned a weight of zero in the correlation.

Table 4. $NaNO_2$ Chenkunova & Protsenko [13]

m (mol/kg)	a(w)	Ø	a(w) (no correction for non-ideality)	Ø (no correction for non-ideality)
0.1000	0.99670	0.9162	0.99670	0.9174
0.2000	0.99351	0.9038	0.99350	0.9050
0.5000	0.98412	0.8886	0.98410	0.8897
0.8000	0.97453	0.8950	0.97450	0.8961
1.0000	0.96804	0.9015	0.96800	0.9026
2.0000	0.93628	0.9137	0.93620	0.9149
3.0000	0.90411	0.9326	0.90400	0.9337
4.0000	0.87184	0.9516	0.87170	0.9527
5.0000	0.84007	0.9673	0.83990	0.9685
6.0000	0.81149	0.9662	0.81130	0.9673
7.0000	0.78232	0.9734	0.78210	0.9745
8.0000	0.75424	0.9785	0.75400	0.9796
9.0000	0.72735	0.9817	0.72710	0.9828
10.0000	0.70077	0.9869	0.70050	0.9879
11.0000	0.67538	0.9903	0.67510	0.9913
12.2500	0.64409	0.9967	0.64380	0.9977

Table 5. KNO_2 Ray & Ogg [12]

m (mol/kg)	a(w)	Ø	a(w) (no correction for non-ideality)	Ø (no correction for non-ideality)
0.2345 *	0.99281	0.8542	0.99280	0.8552
0.4960 *	0.98532	0.8276	0.98530	0.8287
0.4700 *	0.98152	1.1013	0.98150	1.1027
0.9390	0.97144	0.8566	0.97140	0.8577
1.9970	0.94247	0.8235	0.94240	0.8245
4.6400	0.87414	0.8046	0.87400	0.8056
9.5760	0.76523	0.7755	0.76500	0.7764
19.9500	0.61190	0.6033	0.61160	0.6840
31.1800	0.52002	0.5820	0.51970	0.5826

* Assigned a weight of zero in the correlation.

Table 6. KNO_2 Chekhunova & Protsenko [13]

m (mol/kg)	a(w)	ø	a(w) (no correction for non-ideality)	ø
0.1000	0.99670	0.9162	0.99670	0.9174
0.3000	0.99051	0.8820	0.99050	0.8831
0.5000	0.98462	0.8604	0.98460	0.8615
0.7000	0.97893	0.8445	0.97890	0.8455
1.0000	0.97004	0.8443	0.97000	0.8454
3.0000	0.91560	0.8158	0.91550	0.8168
5.0000	0.86275	0.8195	0.86260	0.8204
7.0000	0.81769	0.7980	0.81750	0.7989
10.0000	0.75773	0.7700	0.75750	0.7708
12.0000	0.72285	0.7506	0.72260	0.7514
15.0000	0.67528	0.7265	0.67500	0.7272
17.0000	0.64679	0.7114	0.64650	0.7121
20.0000	0.61230	0.6807	0.61200	0.6814
23.0000	0.58171	0.6538	0.58140	0.6544
27.0000	0.54791	0.6184	0.54760	0.6190
31.0000	0.52082	0.5841	0.52050	0.5846
34.1200	0.50122	0.5618	0.50090	0.5624

Table 7. $RbNO_2$ Chekhunova, Protsenko & Venerovskaya [11]

m (mol/kg)	a(w)	ø	a(w) (no correction for non-ideality)	ø
0.3000	0.99071	0.8633	0.99070	0.8644
0.5000	0.98482	0.8491	0.98480	0.8502
0.7000 *	0.97933	0.8283	0.97930	0.8293
1.0000	0.97054	0.8300	0.97050	0.8311
2.0000	0.94277	0.8178	0.94270	0.8188
3.0000	0.91590	0.8127	0.91580	0.8137
4.0000	0.89062	0.8037	0.89050	0.8047
5.0000	0.86625	0.7970	0.86610	0.7980
7.0000	0.81999	0.7869	0.81980	0.7878
9.0000	0.77752	0.7760	0.77730	0.7769
11.0000	0.74044	0.7582	0.74020	0.7590
13.0000	0.70596	0.7434	0.70570	0.7442
15.0000	0.67688	0.7221	0.67660	0.7229
17.0000	0.64749	0.7096	0.64720	0.7103
19.0000	0.62300	0.6912	0.62270	0.6919
23.0000	0.58011	0.6571	0.57980	0.6577
27.0000	0.54431	0.6252	0.54400	0.6258
31.0000	0.51062	0.6018	0.51030	0.6023
35.0000	0.47862	0.5843	0.47830	0.5848
39.0000	0.44961	0.5689	0.44930	0.5694
43.0000	0.42391	0.5539	0.42360	0.5544
47.0000	0.40110	0.5395	0.40080	0.5399
51.0000	0.37930	0.5276	0.37900	0.5280
55.0000	0.36029	0.5151	0.36000	0.5155
57.0000	0.35189	0.5086	0.35160	0.5090
59.0000	0.34389	0.5021	0.34360	0.5025
61.0000	0.33668	0.4953	0.33640	0.4957
62.3000	0.33288	0.4900	0.33260	0.4904

* Assigned a weight of zero in the correlation.

Table 8. $CsNO_2$ Chekhunova, Protsenko & Venerovskaya [11]

m (mol/kg)	a(w)	ø	a(w) (no correction for non-ideality)	ø
0.1000 *	0.99660	0.9440	0.99660	0.9452
0.3000	0.99051	0.8820	0.99050	0.8831
0.5000	0.98442	0.8717	0.98440	0.8728
0.7000	0.97813	0.8769	0.97810	0.8780
1.0000	0.96904	0.8729	0.96900	0.8740
2.0000	0.93947	0.8664	0.93940	0.8675
3.0000	0.91040	0.8684	0.91030	0.8695
4.0000	0.88263	0.8663	0.88250	0.8673
5.0000	0.85616	0.8621	0.85600	0.8631
7.0000	0.80780	0.8463	0.80760	0.8472
9.0000	0.76273	0.8352	0.76250	0.8362
11.0000	0.72195	0.8220	0.72170	0.8229
15.0000	0.65209	0.7911	0.65180	0.7919
19.0000	0.59531	0.7577	0.59500	0.7584
21.0000	0.57081	0.7410	0.57050	0.7417
23.0000	0.54771	0.7264	0.54740	0.7271
25.0000	0.52792	0.7092	0.52760	0.7099
27.0000	0.50982	0.6925	0.50950	0.6932
29.0000	0.49332	0.6762	0.49300	0.6769
31.0000	0.47902	0.6590	0.47870	0.6595
33.0000	0.46682	0.6407	0.46650	0.6413
35.0000	0.45631	0.6221	0.45600	0.6227
36.0000	0.45171	0.6127	0.45140	0.6132

* Assigned a weight of zero in the correlation.

Table 9. Parameters for the Correlating Equations.

Salt	Parameter	σ	Overall σ of the fit
$LiNO_2$			0.0057
	B 1.42400	0.058	
	C 0.199194	0.0042	
	D -5.53622×10^{-3}	3.7×10^{-4}	
	E 3.31054×10^{-5}	1.1×10^{-5}	
$NaNO_2$			0.0036
	B 0.9282076	0.054	
	C 9.02846×10^{-2}	0.015	
	D -9.69288×10^{-3}	0.003	
	E 5.60276×10^{-4}	3.0×10^{-4}	
	F -1.25644×10^{-5}	1.0×10^{-5}	
KNO_2			0.0048
	B 0.860242	0.022	
	C -1.00624×10^{-3}	0.0025	
	D -4.68744×10^{-4}	1.2×10^{-4}	
	E 7.41098×10^{-6}	2.1×10^{-6}	
$RbNO_2$			0.0041
	B 0.7671597	0.018	
	C -4.47001×10^{-3}	0.0021	
	D -7.50722×10^{-4}	9.9×10^{-5}	
	E 1.75653×10^{-5}	2.1×10^{-6}	
	F -1.23804×10^{-7}	1.5×10^{-8}	
$CsNO_2$			0.0042
	B 1.01567	0.033	
	C 6.16559×10^{-3}	0.0039	
	D -1.62993×10^{-3}	3.2×10^{-4}	
	E 5.04186×10^{-5}	1.2×10^{-5}	
	F -5.66883×10^{-7}	1.5×10^{-7}	

Table 10. $LiNO_2$ Recommended values of $\gamma_\pm$ and Φ at 298.15 K

m (mol/kg)	$\gamma_\pm$	Φ	a_w	ΔG^{ex} (J/kg)
0.001	0.9652	0.9885	0.999964	-0.1
0.002	0.9521	0.9842	0.999929	-0.3
0.003	0.9425	0.9811	0.999894	-0.6
0.004	0.9348	0.9786	0.999859	-0.9
0.005	0.9281	0.9765	0.999824	-1.3
0.006	0.9223	0.9747	0.999789	-1.7
0.007	0.9171	0.9730	0.999755	-2.1
0.008	0.9124	0.9715	0.999720	-2.5
0.009	0.9080	0.9702	0.999685	-3.0
0.010	0.9040	0.9689	0.999651	-3.5
0.010	0.9040	0.9689	0.999651	-3.5
0.020	0.8742	0.9600	0.999303	-9.4
0.030	0.8543	0.9544	0.998969	-16.6
0.040	0.8393	0.9504	0.998631	-24.9
0.050	0.8273	0.9474	0.998295	-33.9
0.060	0.8174	0.9451	0.997959	-43.7
0.070	0.8089	0.9432	0.997624	-53.9
0.080	0.8015	0.9418	0.997289	-64.7
0.090	0.7950	0.9406	0.996955	-75.8
0.100	0.7893	0.9397	0.996620	-87.4
0.1	0.7893	0.9397	0.99662	-87.4
0.2	0.7545	0.9375	0.99327	-217.5
0.3	0.7388	0.9413	0.98988	-363.0
0.4	0.7315	0.9475	0.98644	-515.8
0.5	0.7289	0.9548	0.98295	-671.9
0.6	0.7293	0.9629	0.97940	-828.7
0.7	0.7317	0.9713	0.97580	-984.5
0.8	0.7357	0.9800	0.97215	-1138.1
0.9	0.7409	0.9889	0.96844	-1288.5
1.0	0.7471	0.9979	0.96468	-1435.2
1.0	0.7471	0.9979	0.96468	-1435.2
2.0	0.8391	1.0878	0.92461	-2609.8
3.0	0.9617	1.1723	0.88098	-3144.3
4.0	1.1040	1.2500	0.83514	-2995.0
5.0	1.2625	1.3206	0.78827	-2169.6
6.0	1.4348	1.3844	0.74135	-694.0
7.0	1.6188	1.4414	0.69521	1398.2
8.0	1.8121	1.4919	0.65049	4069.2
9.0	2.0120	1.5360	0.60770	7279.3
10.0	2.2156	1.5739	0.56718	10987.8
11.0	2.4197	1.6058	0.52918	15153.7
12.0	2.6209	1.6318	0.49384	19736.1
13.0	2.8159	1.6521	0.46123	24694.3
14.0	3.0011	1.6669	0.43134	29988.3
15.0	3.1733	1.6763	0.40414	35578.4
16.0	3.3293	1.6806	0.37953	41425.7
17.0	3.4666	1.6797	0.35742	47492.2
18.0	3.5827	1.6739	0.33769	53740.4
19.0	3.6758	1.6634	0.32022	60133.8
(sat.) 19.90	3.7389	1.6500	0.30633	65982.5

Table 11. $NaNO_2$ Recommended values of $\gamma_\pm$ and Φ at 298.15 K

m (mol/kg)	$\gamma_\pm$	Φ	a_w	ΔG^{ex} (J/kg)
0.001	0.9646	0.9882	0.999964	-0.1
0.002	0.9509	0.9836	0.999929	-0.3
0.003	0.9408	0.9802	0.999894	-0.6
0.004	0.9325	0.9774	0.999859	-0.9
0.005	0.9253	0.9750	0.999824	-1.3
0.006	0.9190	0.9729	0.999790	-1.7
0.007	0.9133	0.9710	0.999755	-2.1
0.008	0.9081	0.9693	0.999721	-2.6
0.009	0.9033	0.9676	0.999686	-3.1
0.010	0.8988	0.9662	0.999652	-3.6
0.010	0.8988	0.9662	0.999652	-3.6
0.020	0.8648	0.9549	0.999312	-9.9
0.030	0.8413	0.9471	0.998977	-17.8
0.040	0.8230	0.9412	0.998644	-27.0
0.050	0.8079	0.9363	0.998315	-37.1
0.060	0.7950	0.9323	0.997987	-48.1
0.070	0.7838	0.9288	0.997660	-59.8
0.080	0.7739	0.9257	0.997335	-72.2
0.090	0.7649	0.9230	0.997011	-85.2
0.100	0.7568	0.9206	0.996689	-98.8
0.1	0.7568	0.9206	0.99669	-98.8
0.2	0.7018	0.9055	0.99350	-257.4
0.3	0.6697	0.8985	0.99033	-445.3
0.4	0.6478	0.8950	0.98718	-652.7
0.5	0.6317	0.8934	0.98403	-874.5
0.6	0.6193	0.8930	0.98088	-1107.3
0.7	0.6094	0.8934	0.97772	-1349.1
0.8	0.6014	0.8944	0.97455	-1598.0
0.9	0.5948	0.8957	0.97137	-1852.9
1.0	0.5893	0.8973	0.96819	-2112.9
1.0	0.5893	0.8973	0.96819	-2112.9
2.0	0.5637	0.9180	0.93599	-4870.7
3.0	0.5579	0.9371	0.90366	-7744.6
4.0	0.5572	0.9518	0.87182	-10642.9
5.0	0.5577	0.9623	0.84083	-13540.6
6.0	0.5584	0.9698	0.81087	-16432.4
7.0	0.5591	0.9751	0.78196	-19318.1
8.0	0.5597	0.9793	0.75406	-22198.3
9.0	0.5605	0.9829	0.72706	-25072.3
10.0	0.5616	0.9865	0.70087	-27938.1
11.0	0.5630	0.9902	0.67541	-30792.8
12.0	0.5648	0.9940	0.65066	-33633.4
(sat.) 12.34	0.5654	0.9952	0.64254	-34581.4

Table 12. KNO_2 Recommended values of $\gamma_\pm$ and Φ at 298.15 K

	m (mol/kg)	$\gamma_\pm$	Φ	a_w	ΔG^{ex} (J/kg)
	0.001	0.9644	0.9881	0.999964	-0.1
	0.002	0.9506	0.9834	0.999929	-0.3
	0.003	0.9403	0.9799	0.999894	-0.6
	0.004	0.9318	0.9771	0.999859	-0.9
	0.005	0.9245	0.9746	0.999824	-1.3
	0.006	0.9180	0.9724	0.999790	-1.7
	0.007	0.9121	0.9704	0.999755	-2.2
	0.008	0.9067	0.9685	0.999721	-2.6
	0.009	0.9018	0.9668	0.999687	-3.1
	0.010	0.8971	0.9653	0.999652	-3.7
	0.010	0.8971	0.9653	0.999652	-3.7
	0.020	0.8618	0.9531	0.999313	-10.1
	0.030	0.8369	0.9446	0.998979	-18.2
	0.040	0.8174	0.9379	0.998649	-27.7
	0.050	0.8012	0.9323	0.998322	-38.2
	0.060	0.7872	0.9275	0.997997	-49.6
	0.070	0.7750	0.9233	0.997674	-61.9
	0.080	0.7640	0.9195	0.997353	-74.9
	0.090	0.7541	0.9161	0.997034	-88.5
	0.100	0.7450	0.9130	0.996716	-102.8
	0.1	0.7450	0.9130	0.99672	-102.8
	0.2	0.6815	0.8916	0.99360	-272.7
	0.3	0.6422	0.8757	0.99055	-478.3
	0.4	0.6138	0.8637	0.98754	-709.5
	0.5	0.5918	0.8529	0.98457	-960.9
	0.6	0.5738	0.8576	0.98163	-1228.8
	0.7	0.5587	0.8532	0.97871	-1511.0
	0.8	0.5457	0.8496	0.97581	-1805.6
	0.9	0.5344	0.8465	0.97292	-2111.1
	1.0	0.5243	0.8433	0.97005	-2426.6
	1.0	0.5243	0.8433	0.97005	-2426.6
	2.0	0.4608	0.8284	0.94205	-5981.7
	3.0	0.4256	0.8202	0.91516	-10032.1
	4.0	0.4012	0.8133	0.88933	-14419.5
	5.0	0.3823	0.8077	0.86453	-19070.5
	6.0	0.3666	0.8011	0.84093	-23944.0
	7.0	0.3530	0.7947	0.81838	-29014.4
	8.0	0.3408	0.7875	0.79691	-34265.0
	9.0	0.3298	0.7800	0.77652	-39683.8
	10.0	0.3195	0.7720	0.75716	-45262.6
	11.0	0.3100	0.7637	0.73882	-50994.8
	12.0	0.3009	0.7551	0.72145	-56875.6
	13.0	0.2924	0.7463	0.70501	-62901.0
	14.0	0.2843	0.7372	0.68945	-69067.9
	15.0	0.2765	0.7280	0.67473	-75372.9
	16.0	0.2691	0.7186	0.66081	-81814.1
	17.0	0.2620	0.7092	0.64764	-88389.0
	18.0	0.2552	0.6998	0.63518	-95095.4
	19.0	0.2486	0.6904	0.62337	-101931.3
	20.0	0.2424	0.6810	0.61219	-108894.7
	21.0	0.2364	0.6716	0.60158	-115983.6
	22.0	0.2305	0.6624	0.59152	-123196.1
	23.0	0.2250	0.6533	0.58196	-130530.3
	24.0	0.2197	0.6443	0.57287	-137984.2
	25.0	0.2146	0.6354	0.56422	-145556.8
	26.0	0.2097	0.6266	0.55599	-153243.9
	27.0	0.2049	0.6180	0.54814	-161045.9
	28.0	0.2004	0.6096	0.54066	-168960.3
	29.0	0.1960	0.6013	0.53352	-176985.3
	30.0	0.1918	0.5931	0.52672	-185119.4
	31.0	0.1877	0.5850	0.52024	-193360.0
	32.0	0.1837	0.5771	0.51407	-201708.1
	33.0	0.1799	0.5693	0.50821	-210160.6
	34.0	0.1762	0.5615	0.50266	-218715.2
(sat.)	34.12	0.1753	0.5605	0.50202	-219749.8

Table 13. $RbNO_2$ Recommended values of $\gamma_\pm$ and Φ at 298.15 K

m (mol/kg)	$\gamma_\pm$	Φ	a_w	ΔG^{ex} (J/kg)
0.001	0.9643	0.9880	0.999964	-0.1
0.002	0.9504	0.9833	0.999929	-0.3
0.003	0.9400	0.9798	0.999894	-0.6
0.004	0.9315	0.9769	0.999859	-0.9
0.005	0.9241	0.9744	0.999824	-1.3
0.006	0.9176	0.9721	0.999790	-1.7
0.007	0.9116	0.9701	0.999755	-2.2
0.008	0.9062	0.9682	0.999721	-2.6
0.009	0.9012	0.9665	0.999687	-3.1
0.010	0.8965	0.9649	0.999652	-3.7
0.010	0.8965	0.9649	0.999652	-3.7
0.020	0.8606	0.9525	0.999314	-10.2
0.030	0.8353	0.9437	0.998980	-18.4
0.040	0.8154	0.9367	0.998651	-27.9
0.050	0.7987	0.9309	0.998324	-38.6
0.060	0.7844	0.9259	0.998000	-50.2
0.070	0.7718	0.9214	0.997679	-62.6
0.080	0.7605	0.9175	0.997359	-75.8
0.090	0.7503	0.9139	0.997041	-89.7
0.100	0.7410	0.9106	0.996725	-104.3
0.1	0.7410	0.9106	0.99672	-104.3
0.2	0.6753	0.8876	0.99362	-277.8
0.3	0.6344	0.8736	0.99060	-488.8
0.4	0.6048	0.8636	0.98763	-726.7
0.5	0.5818	0.8561	0.98470	-985.9
0.6	0.5630	0.8500	0.98179	-1262.8
0.7	0.5472	0.8451	0.97891	-1554.8
0.8	0.5337	0.8410	0.97605	-1860.0
0.9	0.5218	0.8374	0.97321	-2177.0
1.0	0.5113	0.8344	0.97038	-2504.7
1.0	0.5113	0.8344	0.97038	-2504.7
2.0	0.4450	0.8167	0.94285	-6210.9
3.0	0.4088	0.8079	0.91637	-10448.5
4.0	0.3840	0.8016	0.89090	-15044.9
5.0	0.3651	0.7959	0.86642	-19919.0
6.0	0.3496	0.7903	0.84295	-25024.3
7.0	0.3364	0.7845	0.82049	-30332.0
8.0	0.3247	0.7783	0.79904	-35822.5
9.0	0.3141	0.7718	0.77859	-41482.2
10.0	0.3045	0.7649	0.75912	-47301.0
11.0	0.2955	0.7577	0.74059	-53271.4
12.0	0.2871	0.7502	0.72299	-59387.7
13.0	0.2791	0.7424	0.70627	-65645.0
14.0	0.2716	0.7345	0.69039	-72039.6
15.0	0.2644	0.7264	0.67532	-78568.1
16.0	0.2576	0.7181	0.66101	-85227.7
17.0	0.2511	0.7098	0.64742	-92015.8
18.0	0.2448	0.7014	0.63451	-98930.0
19.0	0.2389	0.6930	0.62223	-105968.0
20.0	0.2331	0.6847	0.61055	-113127.6
21.0	0.2276	0.6764	0.59941	-120406.5
22.0	0.2224	0.6682	0.58878	-127802.7
23.0	0.2173	0.6602	0.57862	-135313.9
24.0	0.2125	0.6523	0.56889	-142937.8
25.0	0.2078	0.6446	0.55956	-150672.4
26.0	0.2034	0.6371	0.55057	-158515.2
27.0	0.1991	0.6298	0.54191	-166464.0
28.0	0.1951	0.6227	0.53354	-174516.3
29.0	0.1912	0.6159	0.52543	-182669.9
30.0	0.1874	0.6094	0.51754	-190922.2
31.0	0.1839	0.6031	0.50986	-199270.8
32.0	0.1805	0.5971	0.50235	-207713.2
33.0	0.1772	0.5914	0.49500	-216247.0
34.0	0.1741	0.5860	0.48778	-224869.8
35.0	0.1712	0.5809	0.48068	-233578.9
36.0	0.1683	0.5761	0.47368	-242372.1
37.0	0.1656	0.5715	0.46676	-251246.8
38.0	0.1630	0.5673	0.45992	-260200.8
39.0	0.1606	0.5633	0.45315	-269231.6
40.0	0.1582	0.5595	0.44645	-278337.2
41.0	0.1559	0.5561	0.43980	-287515.2
42.0	0.1538	0.5528	0.43321	-296763.7
43.0	0.1517	0.5497	0.42669	-306080.7
44.0	0.1497	0.5468	0.42023	-315464.3
45.0	0.1478	0.5441	0.41385	-324912.8
46.0	0.1459	0.5416	0.40756	-334424.7
47.0	0.1441	0.5391	0.40136	-343998.4
48.0	0.1424	0.5367	0.39527	-353632.9
49.0	0.1407	0.5343	0.38932	-363327.0
50.0	0.1390	0.5320	0.38352	-373079.9
51.0	0.1374	0.5296	0.37789	-382890.8
52.0	0.1358	0.5271	0.37245	-392759.5
53.0	0.1343	0.5246	0.36724	-402685.7
54.0	0.1327	0.5218	0.36229	-412669.5
55.0	0.1312	0.5189	0.35762	-422711.3
56.0	0.1296	0.5157	0.35326	-432811.6
57.0	0.1281	0.5122	0.34927	-442971.4
58.0	0.1265	0.5083	0.34567	-453192.0
59.0	0.1249	0.5040	0.34252	-463474.8
60.0	0.1232	0.4992	0.33985	-473821.8
61.0	0.1216	0.4939	0.33773	-484235.2
62.0	0.1199	0.4880	0.33620	-494717.7
(sat.) 62.30	0.1193	0.4860	0.33587	-497076.3

Table 14. $CsNO_2$ Recommended values of $\gamma_\pm$ and Φ at 298.15 K

	m (mol/kg)	$\gamma_\pm$	Φ	a_w	ΔG^{ex} (J/kg)
	0.001	0.9646	0.9882	0.999964	-0.1
	0.002	0.9509	0.9836	0.999929	-0.3
	0.003	0.9408	0.9802	0.999894	-0.6
	0.004	0.9325	0.9774	0.999859	-0.9
	0.005	0.9254	0.9750	0.999824	-1.3
	0.006	0.9190	0.9729	0.999790	-1.7
	0.007	0.9133	0.9710	0.999755	-2.1
	0.008	0.9081	0.9693	0.999721	-2.6
	0.009	0.9033	0.9676	0.999686	-3.1
	0.010	0.8988	0.9661	0.999652	-3.6
	0.020	0.8647	0.9540	0.999312	-9.9
	0.030	0.8411	0.9469	0.998977	-17.8
	0.040	0.8226	0.9409	0.998645	-27.0
	0.050	0.8073	0.9359	0.998315	-37.2
	0.060	0.7942	0.9316	0.997988	-48.2
	0.070	0.7828	0.9279	0.997662	-60.0
	0.080	0.7726	0.9247	0.997338	-72.4
	0.090	0.7634	0.9218	0.997015	-85.5
	0.100	0.7551	0.9191	0.996694	-99.2
	0.1	0.7551	0.9191	0.99669	-99.2
	0.2	0.6973	0.9016	0.99352	-260.0
	0.3	0.6621	0.8918	0.99041	-452.3
	0.4	0.6371	0.8854	0.98732	-666.6
	0.5	0.6179	0.8808	0.98426	-899.0
	0.6	0.6024	0.8775	0.98121	-1143.1
	0.7	0.5895	0.8749	0.97818	-1399.9
	0.8	0.5785	0.8729	0.97515	-1666.7
	0.9	0.5689	0.8712	0.97214	-1942.3
	1.0	0.5605	0.8700	0.96914	-2225.7
	1.0	0.5605	0.8700	0.96914	-2225.7
	2.0	0.5084	0.8646	0.93959	-5366.4
	3.0	0.4804	0.8632	0.91092	-8870.5
	4.0	0.4610	0.8616	0.88323	-12612.1
	5.0	0.4457	0.8591	0.85662	-16537.1
	6.0	0.4327	0.8555	0.83115	-20617.7
	7.0	0.4211	0.8509	0.80685	-24838.6
	8.0	0.4104	0.8454	0.78374	-29190.5
	9.0	0.4003	0.8391	0.76178	-33667.7
	10.0	0.3907	0.8321	0.74095	-38266.8
	11.0	0.3815	0.8246	0.72122	-42985.2
	12.0	0.3726	0.8166	0.70251	-47821.1
	13.0	0.3641	0.8084	0.68479	-52773.1
	14.0	0.3559	0.7999	0.66799	-57839.8
	15.0	0.3478	0.7912	0.65205	-63019.8
	16.0	0.3401	0.7826	0.63690	-68311.9
	17.0	0.3326	0.7739	0.62250	-73714.5
	18.0	0.3254	0.7652	0.60879	-79226.0
	19.0	0.3185	0.7567	0.59571	-84844.9
	20.0	0.3119	0.7482	0.58322	-90569.4
	21.0	0.3055	0.7399	0.57128	-96397.7
	22.0	0.2993	0.7318	0.55985	-102328.2
	23.0	0.2933	0.7238	0.54891	-108359.2
	24.0	0.2876	0.7159	0.53844	-114489.1
	25.0	0.2820	0.7081	0.52841	-120716.4
	26.0	0.2766	0.7004	0.51884	-127040.0
	27.0	0.2714	0.6927	0.50971	-133459.9
	28.0	0.2663	0.6850	0.50104	-139972.4
	29.0	0.2612	0.6771	0.49286	-146580.4
	30.0	0.2563	0.6691	0.48519	-153283.0
	31.0	0.2514	0.6607	0.47807	-160080.9
	32.0	0.2465	0.6520	0.47155	-166975.4
	33.0	0.2416	0.6427	0.46569	-173968.4
	34.0	0.2366	0.6329	0.46058	-181062.5
	35.0	0.2316	0.6222	0.45628	-188261.0
(sat.)	36.00	0.2265	0.6106	0.45292	-195568.0

Parameters required for fitting the data to the equations and their standard deviations have been summarized for all salts in table 9. The standard deviations of fit ranged from 0.003 to 0.006.

Figures 1–5 are graphs for the five alkali metal nitrites of the experimental ϕ values versus molality and the smoothed curve. In the case of $LiNO_2$, two significantly different curves could be chosen to describe the two sets of data. Figure 1 shows the contrast between the two sets of data.

A somewhat arbitrary choice was made in favor of the vapor pressure measurements of Chekhunova *et al.* [11], based on the following reasons. At the lower concentration, the Ray and Ogg [12] measurements showed a wide scatter and also showed no increase in the osmotic coefficient in the dilute region, where ϕ would be expected to approach a value of 1 according to theory. The data of Chekhunova did show a minimum near 0.2 mol·kg^{-1} while the data of Ray and Ogg did not. In addition the Ray and Ogg data appears to increase slightly at saturation, where another minimum would not normally be expected. Thus the vapor pressure measurements of Ray and Ogg were assigned a weight of zero in this correlation. An overall standard deviation, σ, of 0.006 was obtained using a 4-parameter equation (4) for $LiNO_2$.

The agreement between those two laboratories was better for the $NaNO_2$ data, shown in figure 2 than for the $LiNO_2$ data. The two points for the most dilute solutions from Ray and Ogg [12] were weighted zero because of the large scatter in their data below 0.5 mol·kg^{-1}. It appears that Chekhunova and Protsenko may have performed the 8 measurements below 5 mol·kg^{-1} and the 7 measurements above as separate sets. The $\sigma = 0.004$ for the fit of the $NaNO_2$ data is still quite good however. If the two higher data points at 5 and 6.8 mol·kg^{-1} are omitted from the correlation so that a smoother curve is obtained, a σ of 0.002 is observed.

The K, Rb, and Cs salts appear to exhibit an anomalous behavior (shown in figures 3–5) where an inflection in the values of ϕ as a function of molality occurs below 5 mol·kg^{-1}. Generally the value of ϕ (or $\gamma_\pm$) increases for

most salts as the saturated solution is approached. There is only a single set of experimental data for Rb and Cs nitrite which shows this behavior [11], but a confirming set of measurements [12] for KNO_2 appears to verify this observation.

The parameters and standard deviations for the nitrite salts of Li, Na, K, Rb, and Cs appear in table 9. Again the 3 points of Ray and Ogg [12] for KNO_2 in the most dilute region showed wide scatter and were weighted zero. Similarly, measurements in two dilute solutions of the $RbNO_2$ and $CsNO_2$ data of Chekhunova *et al.* [11] were weighted zero because of the apparent unreliability at the low end of the concentration range where vapor pressure measurements have a larger experimental uncertainty. Again, the osmotic coefficients are shown as a function of molality for K, Rb, and Cs nitrite in figures 3, 4, and 5, respectively.

Figures 6 through 10 show graphs of the deviations of the observed values of ϕ for Li, Na, K, Rb, and Cs nitrite salts, respectively, from the values calculated at the observed concentrations (experimental minus calculated).

The family of curves for the osmotic and mean activity coefficients and the excess Gibbs energy as a function of molality, are illustrated in figures 11, 12, and 13, respectively.

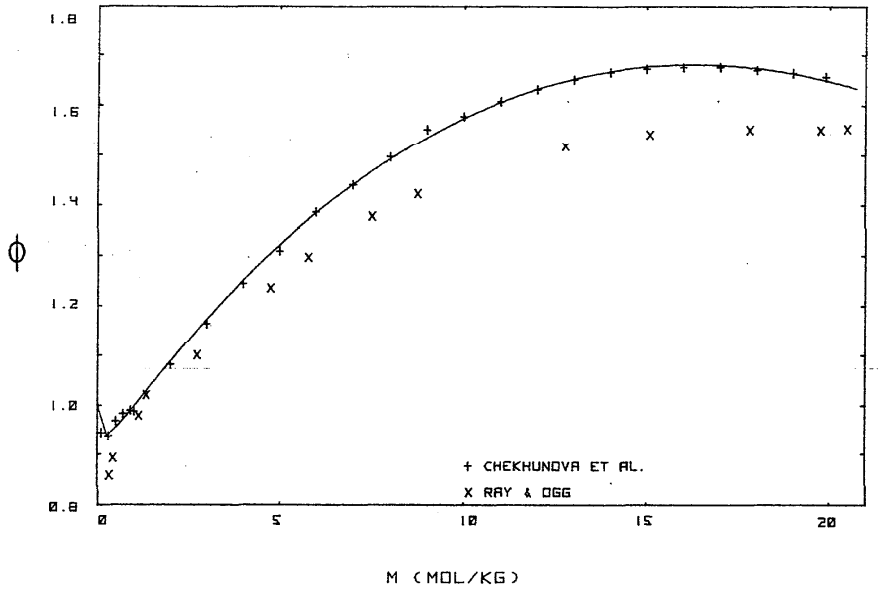

FIGURE 1. Experimental osmotic coefficient vs molality: $LiNO_2$.

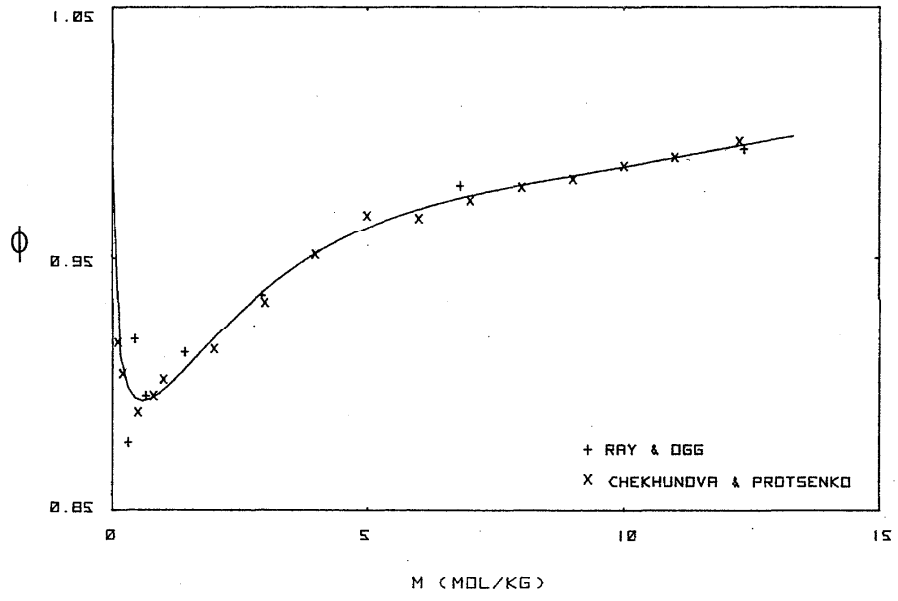

FIGURE 2. Experimental osmotic coefficient vs molality: $NaNO_2$.

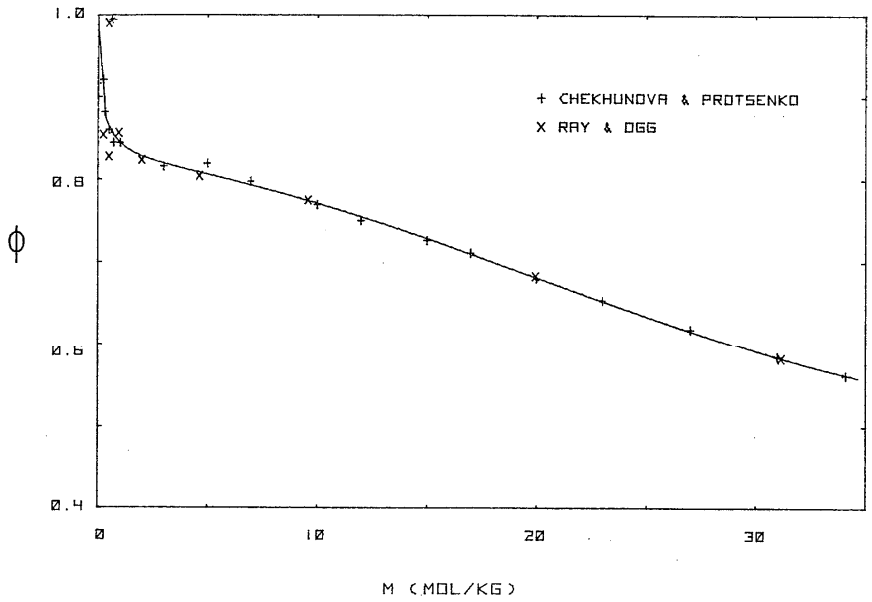

FIGURE 3. Experimental osmotic coefficient vs molality: KNO_2.

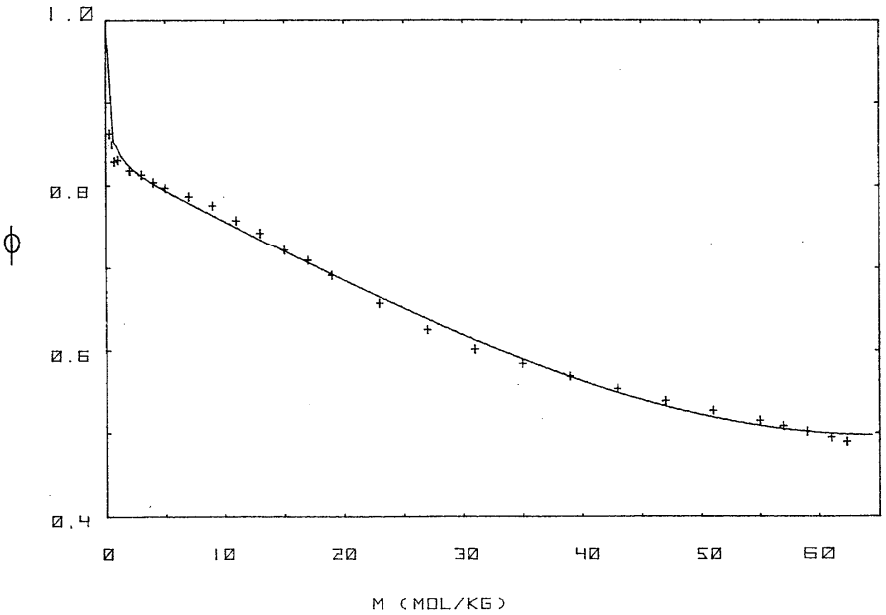

FIGURE 4. Experimental osmotic coefficient vs molality: $RbNO_2$.

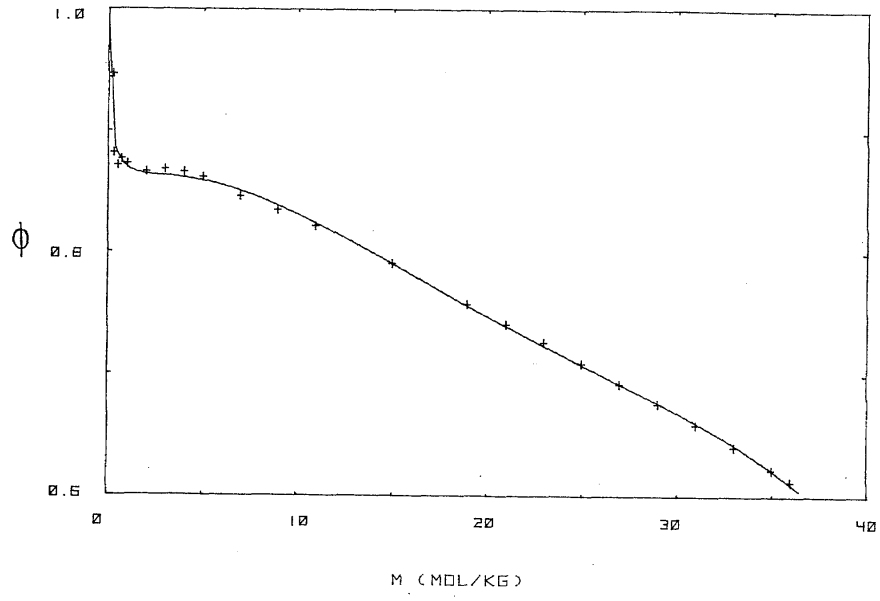

FIGURE 5. Experimental osmotic coefficient vs molality: $CsNO_2$.

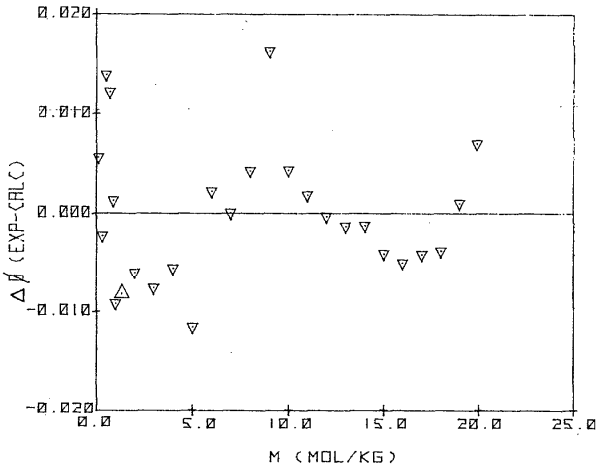

FIGURE 6. Deviation plot: (experimental – calculated) osmotic coefficient vs molality: $LiNO_2$.

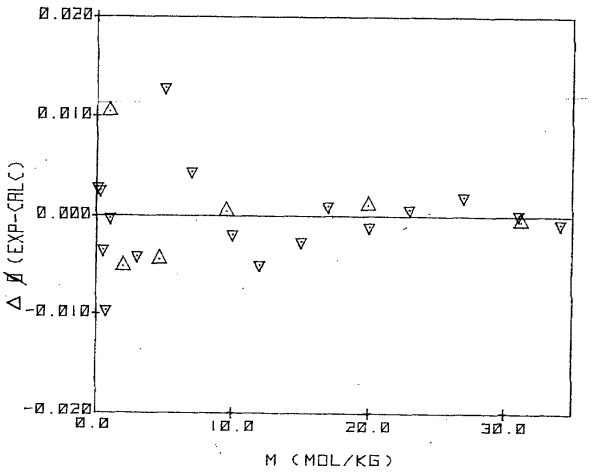

FIGURE 8. Deviation plot: (experimental – calculated) osmotic coefficient vs molality: KNO_2.

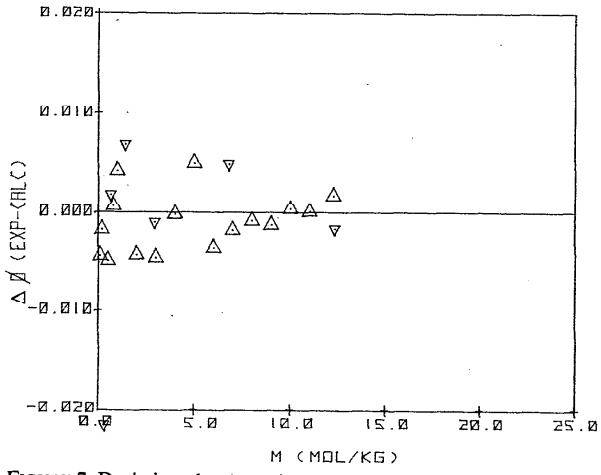

FIGURE 7. Deviation plot: (experimental – calculated) osmotic coefficient vs molality: $NaNO_2$.

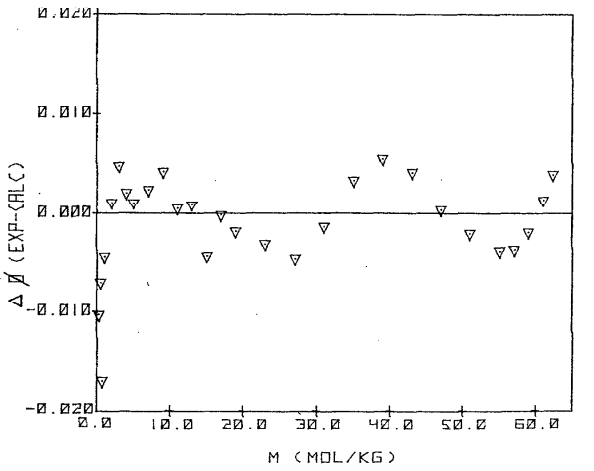

FIGURE 9. Deviation plot: (experimental – calculated) osmotic coefficient vs molality: $RbNO_2$.

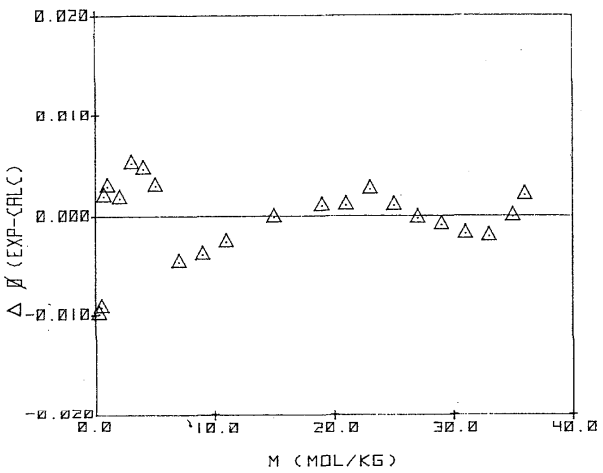

FIGURE 10. Deviation plot: (experimental — calculated) osmotic coefficient vs molality: $CsNO_2$.

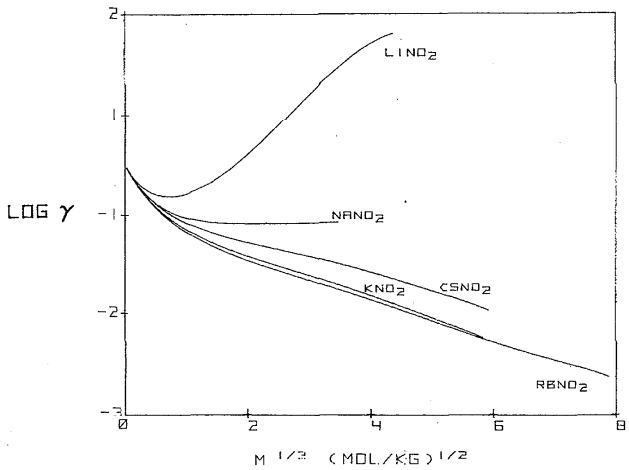

FIGURE 12. Activity coefficients of the alkali metal nitrites vs molality.

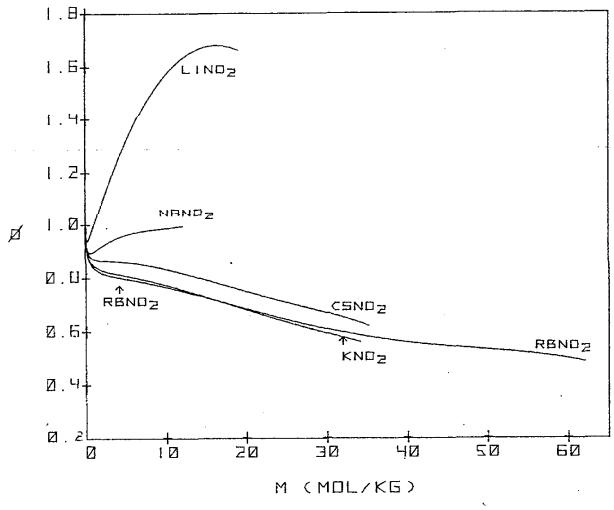

FIGURE 11. Osmotic coefficients of the alkali metal nitrites vs molality.

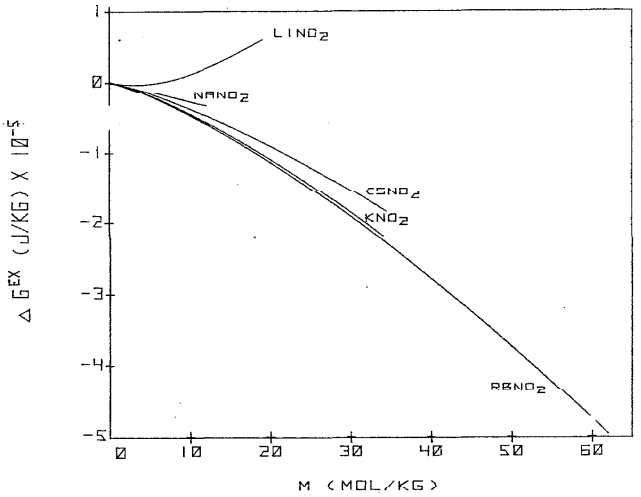

FIGURE 13. Excess Gibbs energy (ΔG^{ex}) of the alkali metal nitrites vs molality.

5. References

[1] Hamer, W. J., and Wu, Y. C., J. Phys. Chem. Ref. Data **1**, 1047 (1972).

[2] Robinson, R. A., and Stokes, R. H., "Electrolyte Solutions," 2nd ed., revised, Butterworth and Co., London, (5th impression, 1970).

[3] Harned, H. S., and Owen, B. B., "The Physical Chemistry of Electrolytic Solution," 3rd ed., Reinhold Pub. Corp., NY (1958).

[4] Pitzer, K. S., and Brewer, L., "Lewis and Randall, Thermodynamics," 2nd ed., McGraw Hill Book Co., Inc., New York, NY (1961).

[5] Staples, B. R., and Nuttall, R. L., J. Phys. Chem. Ref. Data. **6**, 385 (1977).

[6] Staples, B. R., and Nuttall, R. L. "Computer Programs for the Evaluation of Activity and Osmotic Coefficients," NBS Technical Note 928, December 1976.

[7] Staples, B. R., "Activity and Osmotic Coefficients of Aqueous Sulfuric Acid at 298.15 K," J. Phys. Chem. Ref. Data, **10**, 793 (1981).

[8] Goldberg, R. N., Staples, B. R., Nuttall, R. L., and Arbuckle, R., "A Bibliography of Sources of Experimental Data Leading to Activity or Osmotic Coefficients for Polyvalent Electrolytes in Aqueous Solution," NBS Special Publication 485, July 1977.

[9] Stimson, H. F., J. Res. Nat. Bur. Stand. **73A**, 493 (1969).

[10] Keenan, J. H., Keyes, F. G., Hill, P. G., and Moore, J. G., "Steam Tables," Int'l ed. Metric Units, John Wiley & Sons, Inc., New York (1969) p. 148.

[11] Chekhunova, N. P., Protsenko, P. I., and Venerovskaya, L. N., Zhur. Fiz. Khim. **43**, 1158 (1969).

[12] Ray, J. D., and Ogg, R. A., Jr., J. Phys. Chem. **60**, 1599 (1956).

[13] Chekhunova, N. P., and Protsenko, P. I. Zhur. Fiz. Khim. **41**, 2266 (1967).

[14] Linke, W. F., "Solubilities," Amer. Chem. Soc., Washington, DC, 1956.