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Comments

Revised Values of the Osmotic Coefficients and Mean Activity Coefficients of Sodium Nitrate in Water at 25°C

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A paper entitled "Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25° C" appeared in Vol. 1 on pages 1047 to 1100 of this Journal in 1972. Values for NaNO₃ listed in table 23, p. 1071, omitted the data for "Freezing point depression measurements" by Scatchard et al. [10]¹ due to lack of adequate information concerning the apparent molal heat capacity Φ_c . Only recently, Roux et al. [5] have provided values for Φ_c . It is therefore now appropriate to calculate meaningful values for the osmotic coefficients and mean activity coefficients of NaNO₃ in H₂O at 25° C. This Comment also provides corrected values for the molality higher than 6 in response to an informal communication from A.W. Stelson of the California Institute of Technology. The revised values and the parameters are listed in table 1. The original data used for the computations are listed in tables 2 A, B, C, D, and E.

The notation and format for the presentation of the data are those employed previously [1-3].

The auxiliary thermal data used for treating the freezing point depression data are as follows:

$$\Phi_L/J \cdot \text{mol}^{-1} = 1919.1 m^{1/2} - 5033.76 m - 407.671 m^{3/2} \\ + 6585.0 m^2 - 7985.75 m^{5/2} + 4232.12 m^3 \\ - 843.745 m^{7/2} \text{ ref. [4],}$$

and

$$\Phi_c/J \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 30.15 + 38.95 m^{1/2} + 58.5 m \\ - 23.5 m^{3/2} \text{ ref. [5].}$$

Pearce and Hopson [6] reported a solubility of 10.83 mol · kg⁻¹ for NaNO₃ in H₂O at 25° C. This value is in good agreement with those values which may be calculated from the data compiled by Linke and Seidell [7].

¹ Figures in brackets indicate literature references at the end of this paper.

TABLE 1.

Recommended Values for the mean activity and osmotic coefficient of sodium nitrate, NaNO_3 , 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	.9647	.9882	.995964	-0.
.002	.9512	.9837	.995929	-1.
.003	.9412	.9804	.995894	-1.
.004	.9330	.9777	.995859	-1.
.005	.9259	.9753	.995824	-1.
.006	.9197	.9732	.995790	-2.
.007	.9140	.9714	.995755	-2.
.008	.9089	.9697	.995721	-3.
.009	.9041	.9681	.995686	-3.
.010	.8997	.9666	.995652	-4.
.020	.8663	.9556	.995312	-10.
.030	.8431	.9480	.998976	-18.
.040	.8250	.9421	.998643	-27.
.050	.8100	.9372	.998313	-37.
.060	.7972	.9331	.997985	-48.
.070	.7860	.9295	.997658	-59.
.080	.7759	.9263	.997334	-71.
.090	.7669	.9234	.997010	-84.
.100	.7586	.9207	.996688	-98.
.200	.7008	.9026	.993517	-256.
.300	.6646	.8913	.990412	-446.
.400	.6381	.8831	.987353	-659.
.500	.6171	.8765	.984334	-890.
.600	.5997	.8709	.981348	-1137.
.700	.5849	.8661	.978393	-1397.
.800	.5719	.8618	.975466	-1668.
.900	.5603	.8579	.972565	-1951.
1.000	.5499	.8542	.969690	-2243.
1.250	.5276	.8463	.962603	-3010.
1.500	.5091	.8394	.955650	-3825.
1.750	.4934	.8332	.948818	-4682.
2.000	.4797	.8277	.942096	-5575.
2.250	.4676	.8228	.935475	-6502.
2.500	.4568	.8182	.928946	-7458.
2.750	.4470	.8141	.922500	-8443.
3.000	.4381	.8104	.916132	-9454.
3.250	.4300	.8069	.909834	-10488.
3.500	.4225	.8038	.903599	-11545.
3.750	.4156	.8010	.897423	-12623.
4.000	.4092	.7984	.891301	-13721.
4.250	.4033	.7961	.885228	-14838.
4.500	.3978	.7940	.879200	-15972.
4.750	.3926	.7922	.873214	-17123.
5.000	.3878	.7905	.867266	-18289.
5.250	.3833	.7890	.861355	-19471.
5.500	.3790	.7877	.855479	-20667.
5.750	.3750	.7865	.849635	-21876.
6.000	.3712	.7855	.843823	-23098.
6.250	.3676	.7846	.838041	-24332.
6.500	.3643	.7838	.832291	-25578.
6.750	.3611	.7832	.826571	-26835.
7.000	.3580	.7826	.820882	-28103.
7.250	.3551	.7821	.815225	-29382.
7.750	.3497	.7812	.804012	-31967.
8.000	.3471	.7808	.798459	-33274.
8.250	.3447	.7805	.792945	-34590.
8.500	.3423	.7801	.787472	-35915.
8.750	.3400	.7798	.782043	-37248.
9.000	.3378	.7794	.776662	-38589.
9.250	.3356	.7790	.771330	-39939.
9.500	.3335	.7786	.766053	-41296.
9.750	.3314	.7781	.760834	-42661.
10.000	.3293	.7775	.755677	-44034.
10.250	.3273	.7768	.750586	-45414.
10.500	.3253	.7761	.745567	-46802.
10.750	.3233	.7752	.740623	-48198.
10.830 (sat)	.3227	.7749	.739058	-48646.

Estimated Standard Deviations of Values in TABLE 1.

$m/\text{mol} \cdot \text{kg}^{-1}$	$\sigma(\theta)$	$\sigma(\ln\gamma)$	$\sigma(\gamma)$
.001	.0000	.0000	.0000
.010	.0001	.0002	.0001
.100	.0004	.0009	.0007
1.000	.0006	.0024	.0013
2.000	.0006	.0024	.0011
5.000	.0006	.0022	.0009
10.000	.0014	.0027	.0009
10.830	.0022	.0031	.0010

Coefficients of Correlating Equations

Par	Eqs 4.1 [1] ^a		Eqs 3 [2,3]	
	coefficient	$\sigma(\text{coeff})$	coefficient	$\sigma(\text{coeff})$
1	.1205287009+01	.199-01	.1198540545+01	.325-01
2	-.7005454845-01	.323-02	-.1028638450+01	.771-01
3	.5551911790-02	.514-03	.5560513704+00	.751-01
4	-.1922143722-03	.278-04	-.1785647276+00	.362-01
5			.3132636790-01	.851-02
			-.2313089135-02	.780-03

^a The equation used here is based on natural logarithm. See refs. [2,3].

$\sigma(\text{eqs 1}) = .304-02$
 $\sigma(\text{eqs 3}) = .310-02$

TABLES 2 A, B, C, D AND E

Experimental Data Employed in Generation of Correlating Equations

TABLE 2A.

Kangro and Groeneveld [8]. Vapor pressure measurements. Assigned weight is 1.0.

$m/\text{mol} \cdot \text{kg}^{-1}$	$\theta_{298.15}$
1.000000	.8777 ^a
2.000000	.8355
3.000000	.8155
4.000000	.8006
5.000000	.7927
6.000000	.7856
7.000000	.7811
8.000000	.7804
9.000000	.7786
10.000000	.7773

^a Zero weight.

TABLE 2B.

Pearce and Hopson [6]. Vapor pressure measurements. The data for the highest five molalities were weighted unity and the remainder zero.

$m/\text{mol} \cdot \text{kg}^{-1}$	$\theta_{298.15}$
.100000	.9186 ^a
.200000	.9201 ^a
.400000	.9020 ^a
.600000	.8932 ^a
.800000	.8901 ^a
1.000000	.8866 ^a
1.500000	.8841 ^a
2.000000	.8567 ^a
2.500000	.8533 ^a
3.000000	.8410 ^a
4.000000	.8252 ^a
5.000000	.8092 ^a
6.000000	.7964 ^a
7.000000	.7863
8.000000	.7776
9.000000	.7801
10.000000	.7772
10.830000	.7756

^a Zero weight.

TABLE 2C.

Robinson [9], Isopiestic measurements, reference salt is KCl. Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.105200	.9153
.205900	.9027
.207700	.9018
.343100	.8874
.442800	.8770
.523500	.8748
.593500	.8682
.735700	.8619
.877400	.8597
.915900	.8550
1.175000	.8484
1.181000	.8456
1.205000	.8446
1.293000	.8428
1.317000	.8440
1.441000	.8394
1.529000	.8374
1.569000	.8378
1.674000	.8333
1.798000	.8296
1.845000	.8287
2.066000	.8248
2.596000	.8153
2.738000	.8135
2.814000	.8138
2.912000	.8126
2.956000	.8124
3.127000	.8112
3.138000	.8093
3.237000	.8077
3.506000	.8008
3.672000	.7997
3.719000	.7990
3.840000	.7990
3.863000	.7950
4.038000	.7950
4.087000	.7965
4.315000	.7912
4.467000	.7912
4.735000	.7895
5.000000	.7885
5.016000	.7901
5.072000	.7898
5.194000	.7912
5.505000	.7875
5.628000	.7873
5.671000	.7865
5.759000	.7890
6.025000	.7908

TABLE 2D.

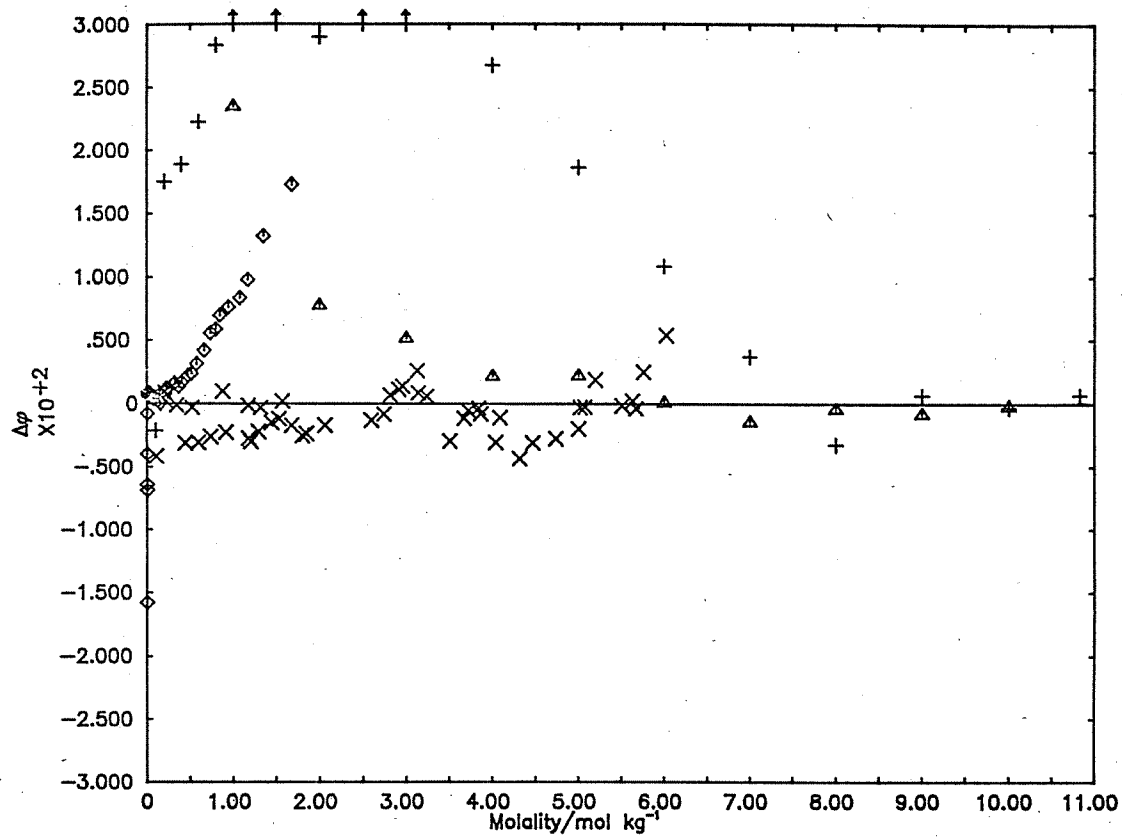
Scatchard Prentiss and Jones [10]. Freezing point depression measurements. ϕ_L data from Parker's evaluation [4] and ϕ_C data from Roux et al. [5] were used in treating these data. The data from 0.000803 to 0.19565 mol·kg⁻¹ were weighted 1.0, those from 0.22017 to 0.57485 mol·kg⁻¹ were weighted 0.5, and the remainder were weighted 0.2.

$m/\text{mol}\cdot\text{kg}^{-1}$	$\phi_{298.15}$
.000803	.9736
.000985	.9819
.002096	.9765
.003101	.9761
.006389	.9717
.010875	.9663
.017605	.9585
.021100	.9552
.036710	.9447
.055233	.9357
.073695	.9286
.093962	.9227
.141630	.9125
.153590	.9097
.195650	.9036
.220170	.9019
.223840	.9007
.249410	.8977
.318100	.8913
.368800	.8868
.404140	.8845
.473850	.8803
.512690	.8781
.574850	.8754
.663380	.8720
.735210	.8701
.796370	.8678
.843710	.8670
.942820	.8639
1.074200	.8601
1.166200	.8586
1.351400	.8566
1.676500	.8523

TABLE 2E.

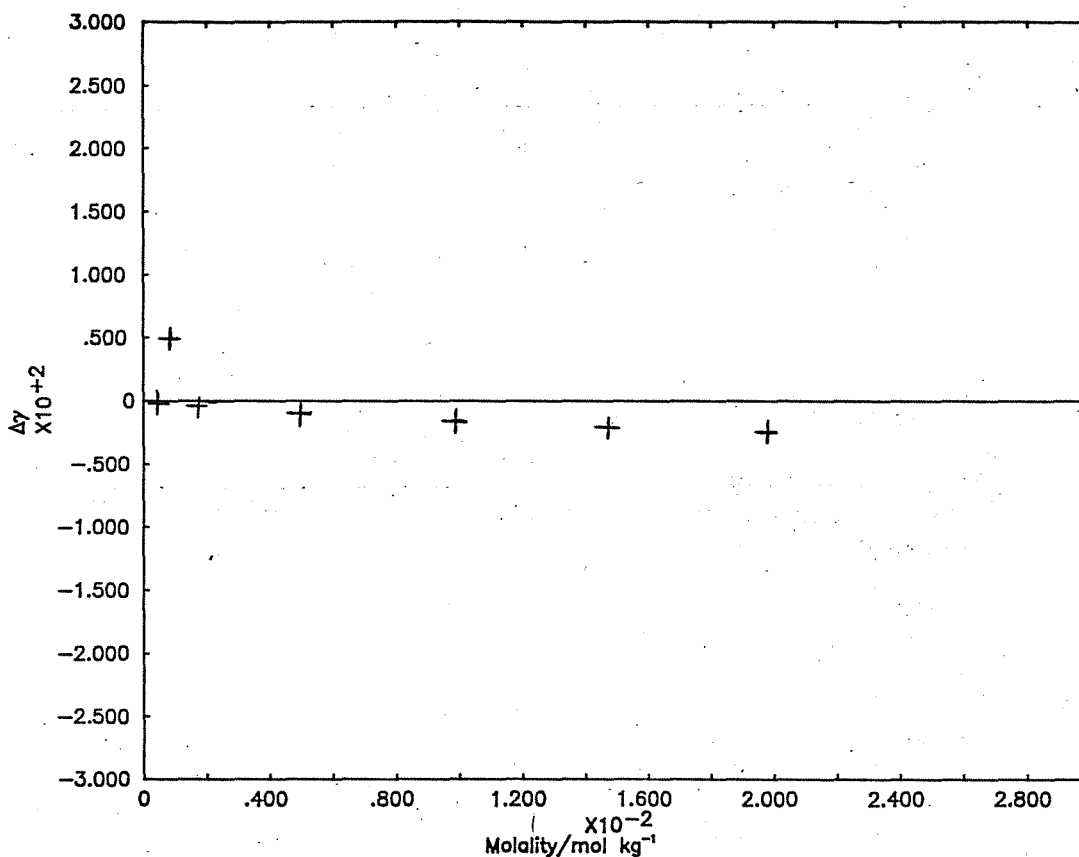
Harned and Shropshire [11, 12]. Activity coefficients based on diffusion measurements. Note that there is an obvious typographical error in ref. [12] for the value of γ at 0.015 mol·kg⁻¹. The value for γ at 0.001 mol·kg⁻¹ given in ref. [11] differs by 0.005 from the value given in ref. [12]. Assigned weight is 1.0.

$m/\text{mol}\cdot\text{kg}^{-1}$	γ
.000500	.9746
.001000	.9696
.002000	.9508
.005000	.9251
.010000	.8983
.015000	.8793
.020000	.8643



Deviation Plot for NaNO_3 : $\Delta\phi$ vs molality

- △ Kangro and Groeneveld [8].
- + Pearce and Hopson [6].
- × Robinson [9].
- ◇ Scatchard, Prentiss, and Jones [10].



Deviation Plot for NaNO₃: Δγ vs molality

+ Harned and Shropshire [11,12]

Acknowledgement

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