

Enthalpy of Solution of Sodium Nitrite

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An adiabatic solution calorimeter was used to measure enthalpies of solution and dilution of sodium nitrite in water in the concentration range of 5 to 200 mmol·kg⁻¹. For the solution reaction where molality, $m = 100$ mmol·kg⁻¹, $\Delta C_p = -1.394 \pm 0.014$ J·g⁻¹·K⁻¹ (-23.0 ± 0.2 cal·mol⁻¹·K⁻¹). Other ΔC_p values for some dilution reactions were also measured. The value selected for the enthalpy of solution at infinite dilution is

$$\begin{aligned}\Delta H_{\infty}^{\circ}(298.15 \text{ K}) &= 14.006 \pm 0.015 \text{ kJ} \cdot \text{mol}^{-1} \\ &= 3.347 \pm 0.004 \text{ kcal} \cdot \text{mol}^{-1}\end{aligned}$$

Values for the relative apparent molal heat content ϕ_L , are tabulated and the enthalpy of transition and of fusion derived from differential thermal analysis measurements are also given.

Key Words: Calorimetry, soln.; NaNO₂, enthalpy of dilution; NaNO₂, enthalpy of soln.; NaNO₂, relative apparent molal heat content; NaNO₂, enthalpies of transition and fusion; NaNO₂, melting temperature.

1. Introduction

In the evaluation of the thermal properties of aqueous univalent electrolyte solutions [1],¹ the tabulation of the relative apparent molal heat content, ϕ_L , of NaNO₂ in H₂O reveals the absence of data for concentrations between 185 mmol·kg⁻¹ and infinite dilution. The only data available for this evaluation was the work of Perreu [2] who measured the enthalpies of solution and dilution at 287 K between 11.87 and 0.188 mol·kg⁻¹. The evaluation of the enthalpy of solution at infinite dilution, $\Delta H_{\infty}^{\circ}$, was based on very limited data from various measurements between 130 and 170 mmol·kg⁻¹ in the temperature range, 291 to 298 K. Therefore, a large uncertainty, 1.2 percent, was assigned to the "best" value for $\Delta H_{\infty}^{\circ}$.

In this work we have measured enthalpies of solution and dilution of NaNO₂ in the dilute region where data were not previously available, as well as in the same concentrations previously measured, for confirmation of earlier work. We have also measured ΔC_p 's for the reactions. These provide more accurate corrections for the earlier work on enthalpy of solution to the standard temperature.

2. The NaNO₂ Sample

The "unpurified" sample was the ACS reagent grade from a commercial source with specifications of purity of at least 97

percent. The method for purification used for this sample was described previously [3]. It consisted of recrystallization from aqueous solution 3 times, filtration through sintered glass, and finally drying at 383 K under vacuum for more than 72 hours. The material was transferred to a glove box with an argon atmosphere where it was crushed and placed in glass-stoppered bottles in a desiccator for storage. The color of the sample was white with a slight yellow tinge.

When a small portion of this material was exposed to the laboratory atmosphere for 17 hours, no significant change in weight was observed. Therefore, calorimetric samples were transferred to the sample holder in the room air.

The purity of the sample was determined by Gaylon Ross, Office of the Director of the Institute for Materials Research, on the basis of its melting behavior, using a differential thermal analysis instrument of high precision which is commercially available. It was estimated that the purity of the NaNO₂ sample was at least 99.9 mol percent providing all of the impurities are liquid soluble and solid insoluble.² The accuracy of the instrument was carefully checked by comparison with melting temperatures of samples of certified high-purity (99.99+ mol%) lead and indium. Using the indium sample as the calibration material, the lead thermogram was analysed (and vice versa); the observed melting temperatures

² The purity analysis of nearly pure materials involves the use of a plot of T_x versus F^{-1} , where T_x is the temperature of the sample and F is the fraction melted. The slope reflects the impurity in the relationship: $T_x = T_p - N_2^2 RT_p^2 (\Delta H_f)^{-1} F^{-1}$. ΔH_f is the enthalpy of fusion, N_2^2 is the mole fraction of the impurity, and T_p is the melting temperature of the pure major component. When $F^{-1} = 1$, $T_x = T_f =$ the melting temperature where an infinitesimal amount of the solid major component is in thermodynamic equilibrium with the liquid. Analysis of the thermograms resulting from the melting of the NaNO₂ samples indicated that the sample temperature did not change, within the sensitivity of the instrument, during the melting process; the slope was zero for the plot of T_x versus F^{-1} . Therefore, $T_x = T_p$, $N_2^2 = 0$, and the NaNO₂ was pure. The instrument does not have the temperature measurement capability of distinguishing between a sample purity of 99.9 and 99.99 mol percent; consequently, 99.9 mol percent is the lower limit of purity.

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

were in error by not more than 0.1 K relative to accepted values and the calculated ΔH_f was in error by less than 2 percent.

From his measurements, Ross also reports the following data (where the uncertainties in the enthalpies are twice the standard deviation of the mean of four measurements): for the solid-solid transition at 436.35 ± 0.20 K (163.2 ± 0.2 °C), $\Delta H = 2.058 \pm 0.126$ kJ·mol⁻¹ (492 ± 30 cal·mol⁻¹); for the solid-liquid transition at the melting temperature, 554.28 ± 0.1 K (281.13 ± 0.1 °C), $\Delta H = 14.16 \pm 0.42$ kJ·mol⁻¹ (3.38 ± 0.10 kcal·mol⁻¹).

A small evolution of gas was observed during heating of the sample to the melting point; however, the loss in sample mass was approximately 0.1 percent which is about the weighing uncertainty for the 10 mg samples. Subsequent reruns of the same samples showed evidence of thermal degradation with each heating, but the first run indicated that the sample was "pure." In view of the apparently high purity of the sample, the calorimetric data reported here are not corrected for sample impurities.

3. Apparatus and Procedures

The platinum-lined adiabatic solution calorimeter used for these enthalpy measurements was described previously [4]. The reactions were endothermic and required the addition of electrical energy during the chemical reaction to prevent a drop in the temperature of the calorimeter vessel as described in an earlier paper [5]. In each experiment the initial and final systems were calibrated electrically;³ details of these procedures and calculations have been given [4].

The experiments described in this paper were completed between October and December 1972. The calorimeter temperature was measured with a quartz-oscillator using an electronic counter with reference to an NBS standard frequency. The quartz-oscillator was calibrated in June 1972 by comparison with a platinum resistance thermometer. The time and calorimeter temperature readings were automatically recorded on punched tape and a typewriter at precisely 100-s intervals throughout an experiment. Rating period slopes were obtained from a least squares fit to a linear equation of 15 to 20 of the time-temperature readings. Extrapolation of these slopes to the time of initiating the electrical heating gave the initial and final temperatures for the reaction. The difference between these temperatures is the corrected temperature rise, ΔT_c (for details, see [4]).

The molecular masses of NaNO₂, 68.9953, and of H₂O, 18.0154, used in the calculations were taken from the 1969 Table of Atomic Weights [6]. For NaNO₂ (c) the density, 2.14 g·cm⁻³ [7] was used in calculating buoyancy corrections, and for the aqueous solutions of NaNO₂ the densities were taken from the International Critical Tables [8]. A density of 0.00118 g·cm⁻³ was used for air under the average atmospheric conditions in this laboratory, 22.5 ± 0.5 °C, 0.10 ± 0.001 MPa (750 ± 10 mm Hg), and a relative humidity of 35 \pm 15 percent. For energy conversions, 4.184 joules = 1 thermochemical calorie.

4. Experimental Results

The composition and calorimetric data are given in tables 1 and 2 for the experiments in which enthalpies of solution and

dilution of NaNO₂ were measured. The Expt. No. is a serial number for experiments with this calorimeter.

In the first three experiments, the NaNO₂ reagent before purification (see sec. 2) was dissolved in water. In Expts. 703 through 714, the purified crystalline sample was dissolved in water. The ΔC_p for the reaction, -1.394 ± 0.014 J·g⁻¹·K⁻¹, was obtained from Expts. 709, 711, and 712 (at 309 K) and Expts. 708, 713, and 714 (at 298 K); the average final concentrations for the two groups are essentially equal. The uncertainty in the ΔC_p is estimated to be 1 percent. An estimate of the experimental imprecision may be obtained from Expts. 703–714 where ΔH_m (298.15 K) = 208.01 ± 0.13 J·g⁻¹. The 0.06 percent uncertainty is at the 95 percent confidence level.

It was desirable to measure the enthalpy at a final concentration of 180 mmol·kg⁻¹ in order to compare our results directly with earlier measurements. However, the volume of the largest of the three interchangeable cylinders for the platinum sample holder (see [4]) was only 2.7 cm³; the maximum amount of the crystalline sample which it contained resulted in a final concentration of less than 120 mmol·kg⁻¹. In order to obtain the desired concentration, it was necessary in Expts. 715–719 to reduce the calorimetric solution from 16.8 to 15.4 moles of H₂O and to compress the sample into a pellet 1.2 cm in diameter, 0.9 cm in depth, and weighing approximately 2.5 g. The remaining space in the sample cylinder was filled with the loose crystalline material. Expts. 720–722 were similar to the above except that the standard amount of water (16.8 moles) was used for the calorimetric solution. In Expts. 732–735, the pelleted sample with no loose crystalline material was used. These experiments showed that reducing the amount of water for the calorimetric solution and pelleting the NaNO₂ sample had no significant effect on the enthalpy of solution calculated at infinite dilution (to be discussed later).

In Expts. 723–731, enthalpies of dilution of aqueous solutions of NaNO₂ in the sample holder were measured. The three aqueous solutions were prepared by mixing weighed amounts of the components as follows: No. 1 was 36.78 wt. percent NaNO₂ ($m = 8.432$ mol·kg⁻¹); No. 2, 18.53 wt. percent ($m = 3.297$ mol·kg⁻¹); and No. 3, 45.47 wt. percent ($m = 12.087$ mol·kg⁻¹). ΔC_p , -1.75 J·g⁻¹·K⁻¹, for the dilution of Soln. No. 1 was obtained from Expts. 724 and 731, and -1.91 J·g⁻¹·K⁻¹, for the dilution of Soln. No. 3, from Expts. 725 and 726. The uncertainty in these measurements is relatively large because of the small amount of energy absorbed by the reaction. Therefore, for all of the dilution experiments (723–731) we used an approximate $\Delta C_p = -1.85 \pm 0.10$ J·g⁻¹·K⁻¹ for the correction to 298.15 K.

In Expts. 738–756, we measured integral and differential enthalpies of solution to provide additional points on the concentration curve.

In table 2, Q reaction is the energy absorbed by the chemical reaction, and Q reaction = $EEE(\Delta T_c) - Q_e$, where EEE is the mean electrical energy equivalent, ΔT_c is the corrected temperature rise, and Q_e is the electrical energy added during the endothermic reaction to prevent a drop in the calorimeter temperature. $\Delta H_m(T)$ is the measured isothermal enthalpy at the concentration, m , and the temperature of reaction (which is the mean temperature of reaction, \bar{T} reaction, and is equal to $-Q$ reaction per gram of NaNO₂ in the sample. The stirring energy correction is calculated from the slopes of the initial and final rating periods. This correction includes primarily the effects of stirring energy and

³ The 0.1- Ω , 10- Ω , and 10-k Ω standard resistors were last calibrated at NBS in June 1969. The last NBS calibration (based on the 1968 NBS volt) of the saturated standard cells was in July 1969. The record of these calibrations over the years indicates consistent trends which provide confidence in the values used.

Table 1. Composition data for the measurements of enthalpies of solution and dilution of NaNO_2 in water.

Expt. No.	Sample mass g	^a Sample description	Sample composition		^b Cal. soln. mass g	Cal. soln. composition	
			H ₂ O mol	NaNO ₂ mol		H ₂ O mol	NaNO ₂ mol
699	2.26647	U	--	0.0328496	302.46	16.7892	--
700	2.19053	U	--	.0317489	302.39	16.7854	--
701	2.40154	U	--	.0348073	302.41	16.7862	--
703	1.68181	C	--	.0243758	302.42	16.7867	--
704	1.59354	C	--	.0230963	302.40	16.7856	--
708	1.82140	C	--	.0263988	302.43	16.7873	--
709	1.84204	C	--	.0266980	302.44	16.7881	--
710	1.78123	C	--	.0258167	302.45	16.7884	--
711	1.83843	C	--	.0266457	302.44	16.7881	--
712	1.81805	C	--	.0263503	302.42	16.7867	--
713	1.78981	C	--	.0259410	302.41	16.7865	--
714	1.90369	C	--	.0275915	302.42	16.7867	--
715	3.32469	PC	--	.0481872	277.45	15.4009	--
716	3.67788	PC	--	.0533062	277.41	15.3987	--
718	3.55066	PC	--	.0514624	277.35	15.3950	--
719	3.76025	PC	--	.0545001	277.45	15.4006	--
720	3.78835	PC	--	.0549074	302.48	16.7901	--
721	3.61263	PC	--	.0523605	302.46	16.7892	--
722	3.73657	PC	--	.0541568	302.41	16.7865	--
723	3.17425	1	0.11139	.016921	287.42	15.9544	--
724	3.23771	1	.11362	.017259	277.38	15.3968	--
725	3.36318	3	.10179	.022166	277.43	15.3995	--
726	3.44047	3	.10413	.022676	277.14	15.3837	--
727	2.91050	2	.13162	.007818	302.46	16.7890	--
728	2.93285	2	.13263	.007878	302.45	16.7886	--
731	3.27278	1	.11485	.017446	277.43	15.3995	--
732	1.49300	P	--	.0216392	277.44	15.4000	--
733	1.50551	P	--	.0218204	277.39	15.3975	--
734	1.51162	P	--	.0219090	302.46	16.7889	--
735	1.50651	P	--	.0218349	302.44	16.7881	--
738	1.19156	C	--	.0172701	302.47	16.7895	--
740	1.20844	C	--	.0175149	302.45	16.7886	--
742	1.23180	C	--	.0178533	302.58	16.7300	0.017209
743	3.52127	PC	--	.0510363	302.68	16.7346	.017458
744	0.54210	C	--	.0078570	302.46	16.7892	--
745	3.49330	PC	--	.0506310	302.22	16.7458	.007837
746	3.53682	PC	--	.0512618	302.48	16.7903	--
747	3.50550	PC	--	.0508078	305.21	16.7457	.051125
748	0.10335	C	--	.0014979	302.43	16.7872	--
751	3.41103	PC	--	.0494386	301.73	16.7429	.001494
752	0.09665	C	--	.0014008	302.49	16.7906	--
753	2.55512	C	--	.0370332	301.79	16.7463	.001397
754	0.10432	C	--	.0015119	302.47	16.7909	--
755	2.58173	C	--	.0374189	302.47	16.7891	.000170
756	2.57355	C	--	.0373004	302.47	16.7891	.000170

^aCode describing sample: U, the crystalline sample before purification; P, pelletized sample; PC, pelletized sample plus loose crystals; C, loose crystals; 1, 2, and 3 are aqueous solutions of NaNO_2 (see text for details).

^bIn the following experiments, the initial calorimetric solution was the final solution from the experiment number given in parentheses: 742 (738), 743 (740), 745 (744), 747 (746), 751 (748), and 753 (752). In Expt. Nos. 755 and 756 the initial solution was from a stock solution which was 0.00381 wt. % NaNO_2 . In all other experiments the initial solution was distilled water.

Table 2. Calorimetric data for the measurements of enthalpies of solution of NaNO_2 in water.

Expt. No.	Electrical energy equivalents		^a Stirring energy correction	Reaction Period	ΔT_c	Q_e	^b -Q reaction	\bar{T} reaction	$\Delta H_m(T)$	^c Corr. to 298.15 K	$\Delta H_m(298.15 \text{ K})$
	Initial	Final									
	$\text{J}\cdot\text{K}^{-1}$	$\text{J}\cdot\text{K}^{-1}$	K	min	K	J	J	K	$\text{J}\cdot\text{g}^{-1}$	$\text{J}\cdot\text{g}^{-1}$	$\text{J}\cdot\text{g}^{-1}$
699	1736.708	1732.549	0.014881	18	0.304035	993.756	466.438	298.5597	205.799	0.571	206.370
700	1737.558	1733.851	.012864	17	.533987	1348.669	421.825	308.5110	192.568	14.44	207.01
701	1735.632	1732.669	.014874	18	.631986	1593.831	497.871	297.9980	207.313	-0.212	207.101
703	1734.699	1732.663	.014844	18	.717747	1593.696	349.352	298.4071	207.743	0.358	208.081
704	1733.731	1731.610	.015520	18	.729057	1595.077	331.861	297.7545	208.254	-0.551	207.703
708	1735.074	1732.732	.016102	18	.700192	1594.294	380.228	297.7758	208.756	-0.522	208.234
709	1737.260	1735.069	.014912	18	.714352	1595.175	354.942	309.1662	192.690	15.36	208.05
710	1735.097	1732.888	.015452	18	.705976	1593.563	369.406	298.6768	207.388	0.734	208.122
711	1737.004	1734.292	.013098	18	.715541	1596.396	354.468	309.1660	192.810	15.36	208.17
712	1736.737	1734.350	.012439	18	.716719	1593.878	349.980	309.1710	192.503	15.36	207.86
713	1734.896	1733.147	.014391	18	.703541	1592.088	372.132	298.1853	207.917	0.049	207.966
714	1735.212	1733.101	.014860	18	.692035	1595.264	395.167	298.3586	207.580	0.291	207.871
715	1632.247	1627.872	.018920	28	.554092	1594.848	692.187	297.9692	208.196	-0.252	207.944
716	1632.442	1628.024	.021918	32	.763477	2012.228	767.633	297.6505	208.716	-0.696	208.020
718	1631.665	1625.475	.017749	18	.681564	1851.769	741.792	297.7919	208.916	-0.499	208.417
719	1631.986	1627.497	.018551	20	.655632	1853.375	784.880	297.8108	208.731	-0.473	208.258
720	1737.288	1731.810	.017210	18	.738584	2068.456	787.347	298.3596	207.834	0.292	208.126
721	1738.439	1732.286	.018661	22	.759738	2070.775	752.354	297.8344	208.256	-0.438	207.818
722	1737.505	1732.071	.016594	25	.744509	2069.979	778.414	297.9716	208.323	-0.249	208.074
723	1680.748	1678.593	.017295	17	.179614	366.614	64.921	298.0995	55.609	-0.093	55.516
724	1643.651	1641.743	.015791	12	.004956	53.702	45.566	308.1082	38.261	18.4	56.7
725	1640.255	1628.938	.016975	17	-.022384	53.696	90.624	298.1167	59.256	-0.062	59.194
726	1640.601	1635.928	.014061	18	.058027	157.543	62.479	308.2330	39.935	18.6	58.6
727	1744.332	1739.797	.016780	17	.078976	154.837	17.255	298.2151	31.991	0.120	32.111
728	1743.896	1746.856	.016229	18	.083874	163.530	17.138	298.2144	31.532	0.119	31.651
731	1739.133	1637.487	.014424	18	.190876	379.601	66.886	298.2099	55.567	0.111	55.678
732	1630.606	1628.153	0.014424	18	0.788107	1594.242	310.116	298.2476	207.713	0.136	207.849
733	1629.900	1628.316	.015054	18	.419007	995.012	312.405	298.2127	207.508	0.087	207.595
734	1736.115	1731.992	.016204	18	.392407	994.463	314.095	298.1400	207.788	-0.014	207.774
735	1734.750	1733.082	.008288	18	.647929	1436.127	312.672	298.2531	207.548	0.144	207.692
738	1734.724	1732.766	.006108	18	.486945	1090.190	245.952	298.8587	206.413	0.988	207.401
740	1734.873	1732.059	.005429	14	.489061	1098.156	250.386	298.2353	207.197	0.119	207.316
742	1729.240	1727.683	.005996	23	.481188	1088.852	257.137	298.2122	208.750	0.087	208.837
743	1732.600	1728.469	.016685	28	.761484	2053.149	735.448	297.7176	208.859	-0.602	208.257
744	1734.808	1730.632	.005597	13	.023138	152.021	111.928	298.1199	206.473	-0.042	206.431
745	1734.075	1728.825	.007290	26	.791632	2098.396	727.724	298.0514	208.320	-0.137	208.183
746	1737.842	1732.789	.015661	20	.659200	1878.524	734.603	298.1803	207.701	0.042	207.743
747	1733.184	1728.339	.017611	23	.668475	1879.272	722.302	298.1900	206.048	0.056	206.104
748	1733.834	1733.292	.006441	15	.077420	155.249	21.036	298.1814	203.557	0.044	203.601
751	1733.672	1728.546	.017796	33	.141827	951.131	710.81	297.9105	208.38	-0.334	208.05
752	1735.371	1732.162	.005098	17	.076192	152.001	19.901	298.1645	205.919	0.020	205.939
753	1732.901	1729.217	.015069	15	.609778	1588.776	533.214	297.6658	208.685	-0.675	208.010
754	1733.809	1732.736	.005605	13	.068942	141.107	21.612	298.2122	207.176	0.087	207.263
755	1736.601	1732.497	.013105	16	.611747	1597.388	536.284	298.0920	207.723	-0.081	207.642
756	1736.132	1732.027	.014180	18	.661020	1594.923	535.366	298.2146	208.026	0.090	208.116

^aThe stirring rate was 250 rpm in Expt. Nos. 735, 738, 740, 742, 744, 745, 748, 752, and 754; 450 rpm in all other experiments.

^bThe following corrections (in J) were made in experiments where the temperature of the vessel was less than that of the shield during a part of the reaction period: No. 699, 0.070; No. 715, 0.542; No. 716, 0.051; No. 719, 0.015; No. 725, 0.340; No. 734, 0.087; No. 743, 0.074; and No. 751, 5.20.

^c $\Delta C_p = -1.85 \pm 0.10 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$ for Expt. Nos. 723 through 731; for all other experiments, $\Delta C_p = -1.394 \pm 0.014 \text{ J}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$.

Table 3. Relative apparent molal heat content of $\text{NaNO}_2 \cdot n \text{H}_2\text{O}$ at 298.15 K [n = moles H_2O (moles NaNO_2) $^{-1}$; m = moles NaNO_2 (kg H_2O) $^{-1}$]

n	m mol·kg $^{-1}$	m $^{1/2}$	ϕ_L		n	m mol·kg $^{-1}$	m $^{1/2}$	ϕ_L	
			J·mol $^{-1}$	cal·mol $^{-1}$				J·mol $^{-1}$	cal·mol $^{-1}$
∞	0.00	0.00	0	0	40	1.3877	1.1780	-623	-149
500,000	.000111	.01054	19	4	37	1.5000	1.2247	-720	-172
100,000	.000555	.02356	42	10	30	1.8503	1.3602	-1016	-243
50,000	.00111	.03332	59	14	27.75	2.0000	1.4142	-1125	-269
20,000	.00278	.05273	93	22	25	2.2203	1.4901	-1289	-308
10,000	.00555	.07450	130	31	22.2	2.5000	1.5811	-1481	-354
7,000	.00793	.08905	151	36	20	2.7753	1.6659	-1659	-396
5,000	.01110	.1054	176	42	18.502	3.0000	1.7321	-1791	-428
4,000	.01388	.1178	193	46	15.859	3.5000	1.8708	-2063	-493
3,000	.01850	.1360	217	52	15	3.7004	1.9236	-2163	-517
2,000	.02775	.1666	252	60	13.88	4.0000	2.0000	-2305	-551
1,500	.03700	.1924	277	66	12.335	4.5000	2.1213	-2523	-603
1,110	.05000	.2236	305	73	12	4.6255	2.1507	-2573	-615
1,000	.05551	.2356	314	75	11.101	5.0000	2.2361	-2724	-651
900	.0617	.2484	318	76	10	5.5508	2.3560	-2916	-697
800	.0694	.2634	326	78	9.5	5.8429	2.4172	-3008	-719
700	.0793	.2816	335	80	9.251	6.0000	2.4495	-3059	-731
600	.0925	.3041	343	82	9.0	6.1674	2.4834	-3105	-742
555.1	.1000	.3162	347	83	8.5	6.5304	2.5554	-3205	-766
500	.1110	.3332	351	84	8.0	6.9385	2.6341	-3305	-790
400	.1388	.3726	356	85	7.9297	7.0000	2.6458	-3318	-793
300	.1850	.4301	347	83	7.5	7.4011	2.7205	-3402	-813
277.5	.2000	.4472	343	82	7.0	7.9297	2.8160	-3489	-834
200	.2775	.5268	305	73	6.938	8.0000	2.8284	-3498	-836
150	.3700	.6083	252	60	6.5	8.5397	2.9223	-3565	-852
111	.5000	.7071	155	37	6.1676	9.0000	3.0000	-3607	-862
100	.5551	.7450	117	28	6.0	9.2514	3.0416	-3628	-867
75	.7401	.8603	-42	-10	5.551	10.0000	3.1623	-3669	-877
55.51	1.0000	1.0000	-272	-65	5.5	11.0924	3.1768	-3674	-878
50	1.1102	1.0536	-372	-89	5.0	11.1016	3.3319	-3707	-886
					4.5	12.3351	3.5121	-3724	-890

vaporization energy (the calorimeter has an opening to the atmosphere). The uncertainty is estimated to be 1 to 5 percent of the correction and contributes significantly to the experimental imprecision.

The length of the reaction periods (table 2) indicates that the reactions were sometimes prolonged when pelleted samples were used. This probably occurred if the pellet remained on the cylinder of the sample holder when opened instead of falling to the bottom of the vessel where the solution was relatively well-stirred.

In several experiments as listed in footnote b of table 2, the rate of electrical heating during the chemical reaction was not sufficient to compensate for the initial rapid absorption of energy. The temperature of the calorimeter vessel dropped below that of the shield and for a brief period adiabatic conditions were not maintained. The method of calculating these corrections has been described previously [4].

5. Relative Apparent Molal Heat Content

The method used to obtain the values of ϕ_L , the relative apparent molal heat content, in the dilute region from $m = 340 \text{ mmol} \cdot \text{kg}^{-1}$ to infinite dilution is the chord area method as described in Harned and Owen [9]. This method involves plotting $\Delta\phi_L (\Delta m^{1/2})^{-1}$ vs. $m^{1/2}$ on a large scale graph. Since

ϕ_L is the negative of the enthalpy of dilution from concentration m to infinite dilution, we may obtain $\Delta\phi_L$ by taking the difference between two enthalpies of solution at concentrations m_1 and m_2 . Numerous short chords were obtained from the integral enthalpies of solution and plotted. A smooth curve was drawn through all the data points. The extrapolation to infinite dilution was made using $472 \text{ cal} \cdot \text{mol}^{-3/2}$ [9] for the limiting value of $d\phi_L (dm^{1/2})^{-1}$. The resultant $d\phi_L (dm^{1/2})^{-1}$ curve was integrated to obtain ϕ_L . These values of ϕ_L were then plotted vs. $m^{1/2}$. The direct measurements of ΔH_{diln} (Expt. Nos. 723-731) were then used with the ϕ_L values previously determined to obtain the ϕ_L values at $m = 8.432, 12.087, \text{ and } 3.297 \text{ mol} \cdot \text{kg}^{-1}$. These values were added to the plot of ϕ_L vs. $m^{1/2}$. A smooth curve joining the two sections was then made. The final smoothed values of ϕ_L are given in table 3 and figure 1.

6. Enthalpy of Solution at Infinite Dilution

Tables 4A and 4B⁴ show the values obtained for $\Delta H_{\infty}^{\circ}$ from the measured values for the enthalpy of solution and the smoothed values for ϕ_L at concentration m . The value for $\Delta H_{\infty}^{\circ}$, $14.006 \text{ kJ} \cdot \text{mol}^{-1}$ ($3.347 \text{ kcal} \cdot \text{mol}^{-1}$), obtained from the table 4A on the purified material, excluded Expt. Nos.

⁴ In these tables, the subscripts *i* and *f* indicate initial and final, respectively.

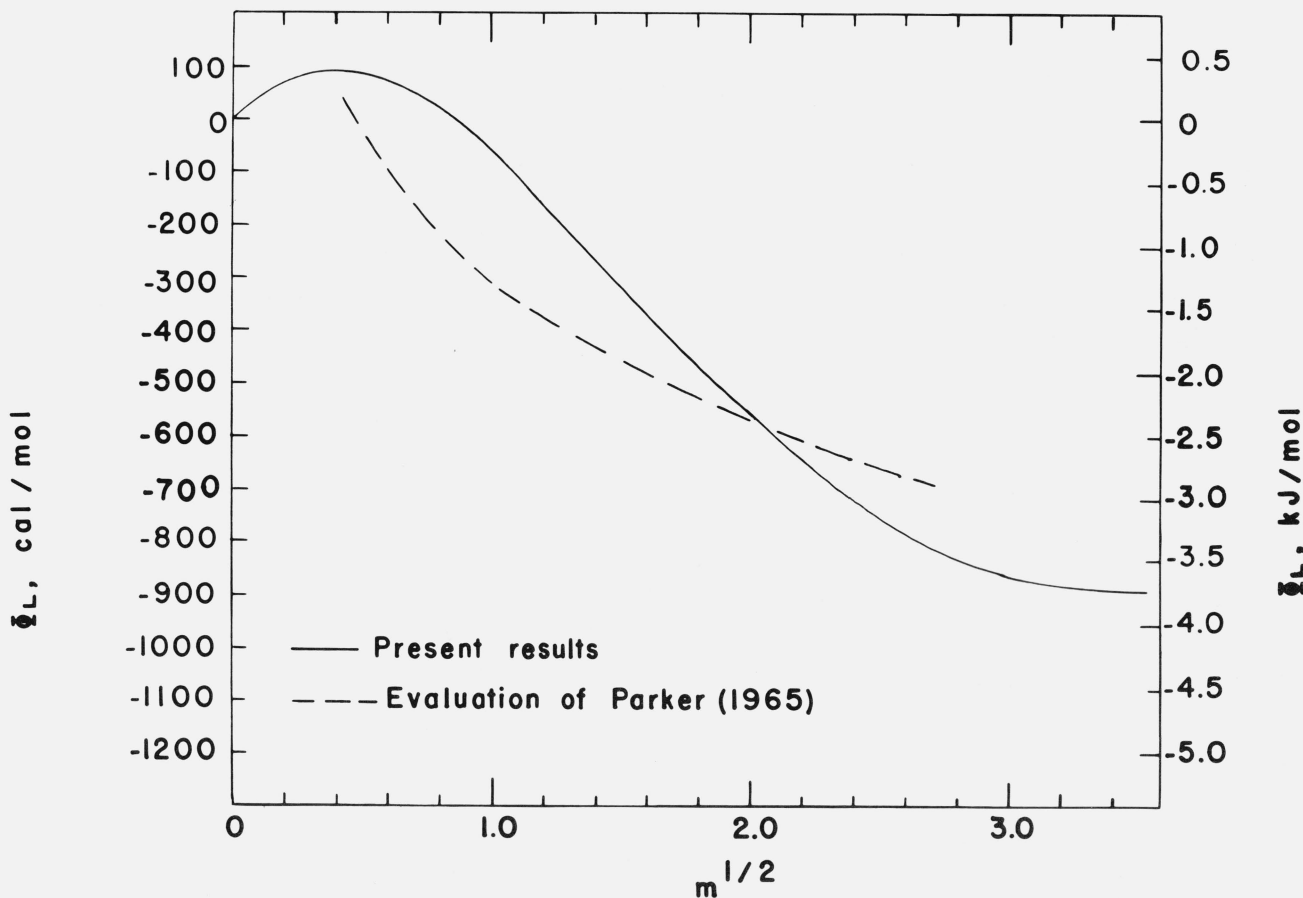


FIGURE 1. Plot showing smoothed values for ϕ_L , the relative apparent molal heat content, of NaNO_2 in H_2O obtained from the present work and from the previous evaluation of Parker [1].

Table 4. The Enthalpy of solution of $\text{NaNO}_2(\text{c})$ in H_2O at infinite dilution at 298.15 K

A. From the integral enthalpies of solution.

Expt. No.	m	$m^{1/2}$	$\Delta H_m(298.15\text{K})$	ϕ_L $\text{J}\cdot\text{mol}^{-1}$	ΔH_∞°	$\Delta H_m(298.15\text{K})$	ϕ_L $\text{cal}\cdot\text{mol}^{-1}$	ΔH_∞°
Unpurified sample:								
699	0.10860	0.3295	14,238.6	349.4	13,889.2	3403.1	83.5	3319.6
700	.10499	.3240	14,282.7	349.4	13,933.3	3413.6	83.5	3330.1
701	.11510	.3393	14,289.0	351.5	13,937.5	3415.2	84.0	3331.2
				(ave.)	13,920.0			3327.0
				(sdm)	± 15.4			± 3.7
Purified sample:								
703	0.08060	0.2839	14,356.6	336.8	14,019.8	3431.3	80.5	3350.8
704	.07637	.2764	14,330.5	334.7	13,995.8	3425.1	80.0	3345.1
708	.08729	.2954	14,367.2	342.2	14,024.8	3433.8	81.8	3352.0
709	.08827	.2971	14,354.5	343.1	14,011.4	3430.8	82.0	3348.8
710	.08536	.2921	14,359.4	341.0	14,018.4	3432.0	81.5	3351.5
711	.08810	.2968	14,362.8	343.1	14,019.7	3432.8	82.0	3350.8
712	.08713	.2952	14,341.4	342.2	13,999.2	3427.7	81.8	3345.9
713	.08578	.2928	14,348.7	341.0	14,007.7	3429.4	81.5	3347.9
714	.09123	.3020	14,342.1	343.9	13,998.2	3427.8	82.2	3345.6
715	.17369	.4167	14,347.2	349.4	13,997.8	3429.0	83.5	3345.5
716	.19215	.4384	14,352.4	343.1	14,009.3	3430.3	82.0	3348.3
718	.18555	.4308	14,379.8	347.3	14,032.5	3436.8	83.0	3353.8
719	.19643	.4432	14,368.8	343.1	14,025.7	3434.2	82.0	3352.2
720	.18152	.4261	14,359.7	347.3	14,012.4	3432.0	83.0	3349.0
721	.17311	.4161	14,338.5	349.4	13,989.1	3427.0	83.5	3343.5
722	.17909	.4232	14,356.1	347.3	14,008.8	3431.2	83.0	3348.2
732	.07800	.2793	14,340.6	334.7	14,005.9	3427.5	80.0	3347.0
733	.07866	.2805	14,323.1	334.7	13,988.4	3423.3	80.0	3343.0
734	.07244	.2691	14,335.4	330.5	14,004.9	3426.2	79.0	3347.2
735	.07219	.2687	14,329.8	330.5	13,999.3	3424.9	79.0	3345.9
738	.05710	.2389	14,309.7	313.8	13,995.9	3420.1	75.0	3345.1
740	.05791	.2406	14,303.8	313.8	13,990.0	3418.7	75.0	3343.7
744	.02598	.1612	14,242.8	246.0	13,996.8	3404.1	58.8	3345.3
746	.16947	.4117	14,333.3	349.4	13,983.9	3425.7	83.5	3342.2
748	.00495	.0704	14,047.5	122.6	*13,924.9	3357.4	29.3	*3328.1
752	.00463	.0680	14,208.8	118.8	*14,090.0	3396.0	28.4	*3367.6
754	.00500	.0707	14,300.2	123.4	*14,176.8	3417.8	29.5	*3388.3
				(ave.)	14,005.6			3347.5
				(sdm)	± 2.7			± 0.6
* Excluded from average.								

Table 4. (cont.)

B. From the differential enthalpies of solution; purified sample.

Expt. No.	m_i	m_f	$m_i^{1/2}$	$m_f^{1/2}$	ΔH_{diff}	$\Delta H_{int, m_f}$	ΔH_{diff}	$\Delta H_{int, m_f}$	ϕ_L, m_f	ΔH°
742 (738)	0.05710	0.11633	0.2390	0.3411	14,408.8	14,360.1	3443.8	3432.1	84.0	3348.1
743 (740)	.05791	.22718	.2406	.4766	14,368.8	14,352.2	3434.2	3430.2	79.0	3351.2
745 (744)	.02598	.19380	.1612	.4402	14,363.6	14,347.4	3433.0	3429.1	82.0	3347.1
747 (746)	.16947	.33788	.4117	.5813	14,220.2	14,277.0	3398.7	3412.3	64.0	3348.3
751 (748)	.00495	.16886	.0704	.4109	14,354.5	14,345.2	3430.8	3428.6	84.0	3344.6
753 (752)	.00463	.12738	.0680	.3569	14,351.7	14,346.1	3430.1	3428.8	84.5	3344.3
755	.000562	.12428	.0237	.3525	14,326.3	14,325.2	3424.1	*3423.8	84.0	3339.8
756	.000562	.12439	.0237	.3520	14,359.0	14,357.6	3431.9	*3431.6	84.0	3343.6
									avg. =	3347.3
*Calculated using $\Delta H_m(298.15 K)(m_1 = 0.562 \text{ mmol} \cdot \text{kg}^{-1}) = 3357$					$cal \cdot mol^{-1}$					

Table 5. Enthalpies of dilution at 298.15 K

Expt. No.	m		$m^{1/2}$		ϕ_L		ΔH_{diln}	
	initial	final	initial	final	initial	final	calc	meas
					$cal \cdot mol^{-1}$		$cal \cdot mol^{-1}$	
727	3.297	0.02565	1.8158	0.1601	-468	58.6	526.6	529.5
728	3.297	.02584	1.8158	.1608	-468	58.6	526.6	521.9
723	8.432	.05846	2.9038	.2418	-849	75.0	924.0	915.5
724	8.432	.06177	2.9038	.2485	-849	75.5	924.5	934.7
731	8.432	.06242	2.9038	.2498	-849	76.0	925.0	918.1
725	12.087	.07937	3.4766	.2817	-890	80.0	970.0	976.1
726	12.087	.08127	3.4766	.2851	-890	81.0	971.0	966.1

748, 752, and 754 because of relatively large experimental uncertainties; Expt. Nos. 755 and 756 of table 4B were also excluded since the enthalpy of solution for the initial solutions where $m = 0.562 \text{ mmol} \cdot \text{kg}^{-1}$ had not been experimentally determined. The total or integral enthalpies of solution shown in table 4B were obtained from the combination of the experimental ΔH_m (298.15 K) of NaNO_2 (c) at the initial concentration and the measured differential enthalpy of solution.

As is evident from the values for the purified sample in table 4A, ΔH_∞ is not dependent upon the form (pelleted or loose) of the sample used. However, the unpurified sample results in $\Delta H_\infty = 13.920 \text{ kJ} \cdot \text{mol}^{-1}$ (3.327 kcal $\cdot \text{mol}^{-1}$) which is 0.6 percent less than that for the purified sample.

Table 5 shows the agreement obtained between the calculated enthalpies of dilution, $\phi_{L_f} - \phi_{L_i}$, and the measured values.

7. Discussion

Parker [1] tabulated the ϕ_L values based on Perreu's [2] measurements of ΔH_{dilin} (287 K, $m = 11.87$ to $0.19 \text{ mol} \cdot \text{kg}^{-1}$) which she corrected to 298.15 K using the tabulated ϕ_C values for NaNO_2 (aq). Our own measurements of $\Delta C_p = -1.85 \pm 0.1 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ ($-30.5 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{deg}^{-1}$) for the dilution are in reasonable agreement with those she used; therefore we have plotted the values of ϕ_L as tabulated by Parker in figure 1 as well as those calculated here. Parker assumed $\phi_L = 40 \text{ cal} \cdot \text{mol}^{-1}$ at the mole ratio, $n_{\text{H}_2\text{O}} = 300$; our value is $83 \text{ cal} \cdot \text{mol}^{-1}$. As is evident, the values are not in agreement, nor will a shift of $43 \text{ cal} \cdot \text{mol}^{-1}$ bring the two curves into better agreement.

Table 6 summarizes the values for ΔH_∞ (298.15 K) obtained from various investigations corrected to 298.15 K where necessary and using the presently obtained values for ϕ_L .

Table 6. Literature values for ΔH_∞° of NaNO_2 (c) in H_2O

Source	T of Meas.	Concentration Range	ΔH_∞° (298.15 K)
	K	$\text{mol} \cdot \text{kg}^{-1}$	$\text{cal} \cdot \text{mol}^{-1}$
Perreu [2]	287	0.14 to 0.22	3303
Bureau [7a]	293	0.14	3367
Matignon and Marchal [11]	293	0.16	3319
Dode [12]	285	0.13	3150
Swietoslowski [13]	291	0.16	3298
Reshetnikov [14]	298	0.07	^a 3300
Wu et al [15]	298	0.04 to 0.007	^b 3262
This work	298	0.005 to 0.20	3347 \pm 17

^aMeasurements in mechanical mixtures of NaOH (c) and NaNO_2 (c).

^bMeasurements in dilute NaOH solutions.

Our own measurements for $\Delta C_p = -1.394 \pm 0.014 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ ($-23.0 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) at $m = 100 \text{ mmol} \cdot \text{kg}^{-1}$ indicate that the absolute value for ϕ_{C_p} tabulated by Parker is too negative by $4 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{deg}^{-1}$. We have made the adjustment for this in correcting those measurements not at 298.15 to 298.15 K. The "best" value for ΔH_∞° (298.15 K) NaNO_2 (c) would now appear to be $14.0056 \pm 0.0076 \text{ kJ} \cdot \text{mol}^{-1}$ ($3.347 \pm 0.002 \text{ kcal} \cdot \text{mol}^{-1}$) with the uncertainty at the 99 percent confidence level. However, we have increased the over-all uncertainty to $\pm 0.015 \text{ kJ} \cdot \text{mol}^{-1}$ ($\pm 0.004 \text{ kcal} \cdot \text{mol}^{-1}$) to include an uncertainty in the extrapolation to infinite dilution.

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