

ENTHALPIES OF CRYSTALLIZATION AND DISSOLUTION OF AMMONIUM BROMIDE IN WATER AT 298.15 K

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ABSTRACT

The enthalpy of dissolution of ammonium bromide in water at 298.15 K was measured over the concentration range 0.01–7.2 mol NH₄Br/1 kg water using three different calorimeters in two laboratories. The results obtained at low concentrations are compared with published values. The concentration dependence of the differential enthalpy of dissolution near saturation is best fitted by the equation

$$-\Delta H = 19.3889 - 2.0654m^{1/2}$$

($m > 6.25$ mol NH₄Br/1 kg H₂O). The enthalpy of crystallization at the saturation concentration 7.968 mol NH₄Br/1 kg H₂O was found to be 13.55 ± 0.05 kJ mol⁻¹. This result is compared with values calculated from published solubility data and from the concentration dependence of the osmotic coefficient at saturation.

INTRODUCTION

Few data are available on the concentration dependence of the enthalpy of dissolution of ammonium bromide in water, particularly in the salt-rich region. Previous measurements, confined to highly dilute solutions, were reviewed by Parker [1], who recommended $-\Delta H^\infty = 16.778 \pm 0.418$ kJ mol⁻¹ as the "best available value" of the first enthalpy of dissolution. This recommendation was based largely on two discordant values of Thomsen [2], 17.0 kJ mol⁻¹ (from four measurements in 1877), and of Fedorov and Silchenko [3], 16.4 kJ mol⁻¹ (from three measurements in 1937). Stephenson et al. [4] measured 16 values of the integral enthalpy of dissolution, ΔH^{in} , over the molality range 0.009–0.055, and their data were least-squares fitted to give (in kJ mol⁻¹):

$$-\Delta H^{\text{in}} = (16.767 \pm 0.031) + (1.649 \pm 0.188)m^{1/2} \quad (1)$$

The initial slope, $d\Delta H^{\text{in}}/dm^{1/2} = 1.649$, is smaller than the theoretical Debye–Hückel value of 1.975 for uni-univalent salts. The first enthalpy of

dissolution given by Beggerow [5], $-\Delta H^\infty = 16.3 \text{ kJ mol}^{-1}$, is the value quoted by Coulter [6] and is not considered since, in fact, it is based on the above mentioned measurements of Fedorov and Silchenko [3]. No data have been published for more concentrated solutions.

Therefore, we decided to measure only a few values of the integral enthalpy of dissolution for $m < 0.1$ and to focus our attention on the measurement of the differential enthalpy of dissolution over the whole concentration range up to nearly saturated solutions. In order for comparison to be made with results for other systems, the measurements were carried out at 298.15 K.

EXPERIMENTAL

Ammonium bromide of analytical grade (Laborchemie Apolda, GDR) was recrystallized twice, dried, and stored over P_2O_5 . All solutions were made up in water redistilled in a quartz apparatus.

The following calorimeters were used for the dissolution experiments. (a) A normal temperature precision calorimeter system [7] (denoted further as NTK), in which about 0.2 g of the salt was dissolved in 70 g of solution or water. The criterion for judging the reliability of measurements was constancy of heat exchange coefficients calculated from the slope of the resistance–time ($R-t$) plot and from heating and cooling curves before and after electrical calibration (heating with a constant power input up to thermal equilibrium). (b) A twin microcalorimeter of our own design [8] with Dewar-type cells (denoted further as T), in which 0.01 to 0.25 g of the salt was dissolved in 180 cm^3 of solution or water. The digital output data were processed using the Regnault–Pfaundler method [9]. (c) A medium temperature Calvet calorimeter (Setaram, France) with mixing facilitated by rocking (denoted further as C), in which 0.05–0.07 g of the salt was dissolved in 10 cm^3 of solution or water. All the calorimeters were calibrated against standard reference materials [10].

A relative molar mass of NH_4Br of 97.94246 was used for all calculations.

RESULTS AND DISCUSSION

For low molalities of the final solutions ($m_2 < 0.07 \text{ m}$), pure ammonium bromide was dissolved in water to determine the integral enthalpies of dissolution (ΔH^{in}). In addition, three enthalpies were measured for dissolution of the salt in solutions of initial concentrations within the range 0.01–0.07 mol $\text{NH}_4\text{Br}/1 \text{ kg H}_2\text{O}$, and these values were converted to the integral enthalpies of dissolution for the final solution concentrations by the use of eqn. (1). The results obtained are summarized in Table 1 and compared with those given by Stephenson et al. [4] in Fig. 1.

TABLE 1

Integral dissolution enthalpies of ammonium bromide in water in diluted solutions

Molality mol NH ₄ Br/1 kg H ₂ O		Amount of salt dissolved (g)	$m_2^{1/2}$	Calorimeter	$-\Delta H^m$
Initial m_1	Final m_2				
0.00000	0.02554	0.150276	0.159807	NTK	16.897
0.00000	0.00852	0.050134	0.092294	NTK	17.021
0.00000	0.00500	0.039101	0.070732	NTK	17.197
0.00000	0.05138	0.050011	0.226675	C	16.887
0.00000	0.00929	0.156232	0.096383	T	17.066
0.00000	0.00496	0.083327	0.070414	T	17.112
0.00000	0.00179	0.030171	0.042340	T	16.885
0.00000	0.00146	0.024576	0.038240	T	16.751
0.00000	0.00088	0.014837	0.029729	T	16.767
0.00000	0.00067	0.011307	0.025935	T	16.529
0.01707	0.05123	0.200943	0.226340	NTK	16.972
0.05123	0.08532	0.200527	0.292096	NTK	17.229
0.06820	0.10255	0.202100	0.320234	NTK	17.136

Of the thirteen values measured by us, four deviate markedly from the correlation of Stephenson et al. [4]. Since our instrumentation is more suitable for measurements in more concentrated solutions, our values for the region of dilute solutions are expected to show a higher scatter compared to the results of Stephenson et al. [4], apparently the most reliable data available.

The concentration dependence of the integral enthalpy of dissolution measured by us in the region below 0.07 m gives $\Delta H^\infty = -16.826 \text{ kJ mol}^{-1}$, whereas the first enthalpy of dissolution derived from the measurements of Stephenson et al. [4] by means of eqn. (1) is $-16.767 \text{ kJ mol}^{-1}$.

The uncertainty in the value of ΔH^∞ recommended by Parker [1] is 600 J, whereas the data of Stephenson et al. [4] exhibit a very low standard deviation, which for $m=0$ amounts to about 30 J. The mean standard deviation of our data from a least-squares fit is about 135 J, corresponding to an uncertainty of $\pm 1\%$.

Virtually no data have been published for the integral or differential enthalpy of dissolution of NH₄Br in water in the range of more concentrated solutions, including the region approaching the saturation concentration (m_s). Our data for the enthalpy of dissolution at $m > 0.08$ are presented in Table 2, together with their deviations from the best-fit curve represented by the equation

$$-\Delta H = 17.1468 - 0.0591m^{1/2} - 0.42985m, \text{ for } 0.08 < m = m_s \quad (2)$$

Also included in Table 2 are the relative changes in the concentration produced by salt dissolution. For about half of the experiments, this change

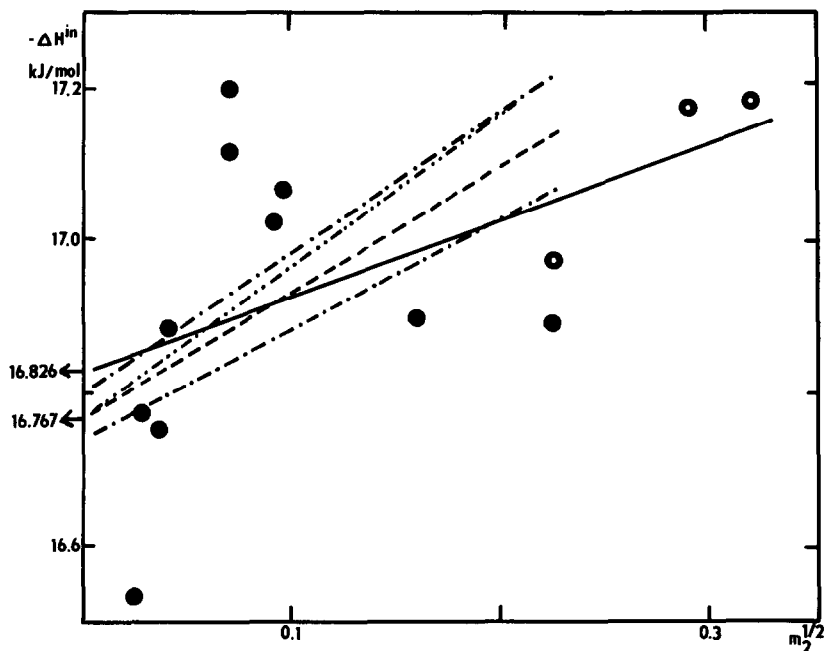


Fig. 1. Integral enthalpies of dissolution of ammonium bromide in water at 298.15 K for final concentrations $m_2 < 0.11$ mol $\text{NH}_4\text{Br}/1$ kg H_2O . (●) Our data for dissolution of salt in water; (○) data recalculated by means of eqn. (1). (-----) Correlation data of Stephenson et al. [4]; (---) uncertainty limit of the data of Stephenson et al. [4]; (—) least-squares fit of our data; (····) theoretical Debye-Hückel plot of the concentration dependence of the enthalpy of dissolution for uni-univalent salts.

was lower than 2%, so that the measured data can be considered as pseudo-differential enthalpies of dissolution. The concentration changes for individual experiments are illustrated in Fig. 2. Even though some measurements, especially in the region of dilute solutions, involved non-negligible concentration changes, the data evaluated for the arithmetic means of the initial and final concentrations are also taken as pseudo-differential, because the scatter in the measured values exceeds possible corrections for the non-differential experimental conditions. Thus, the regression parabola in Fig. 2 can be considered as a realistic estimate of the concentration dependence of the differential enthalpy of dissolution.

The maximum relative deviation of experimental values from those calculated on the basis of eqn. (2), $\Delta r = (\Delta H_{\text{exp}} - \Delta H_{\text{calc}}) / \Delta H_{\text{calc}}$, is 3.2%. It is worth noting that the scatter of the data decreases with increasing concentration.

The available data for the saturation concentration at 298.15 K from five sources are summarized in Table 3. The data differ insignificantly, the maximum relative difference being 1.85%. Considering the readiness of

TABLE 2

Enthalpies of dissolution of ammonium bromide in its aqueous solutions at 298.15 K

mol NH ₄ Br/1 kg H ₂ O		Relative concentra- tion change (%)	Mean concentra- tion	Type of calor.	- Δ <i>H</i> (kJ mol ⁻¹)	Δ <i>r</i>
Initial <i>m</i> ₁	Final <i>m</i> ₂					
0.08532	0.11940	33.293	0.10236	NTK	16.876	-1.22
0.09949	0.14965	40.266	0.12457	NTK	17.362	1.70
0.11940	0.15344	24.953	0.13642	NTK	16.891	-1.03
0.18746	0.22149	16.641	0.20447	NTK	17.096	0.37
0.20029	0.23430	15.653	0.21730	NTK	17.019	-0.04
0.29990	0.33395	10.743	0.31693	NTK	17.067	0.53
0.34569	0.39681	13.771	0.37125	C	16.609	-2.02
0.34569	0.41285	17.709	0.37927	C	16.777	-1.01
0.40009	0.43412	8.160	0.41711	NTK	16.678	-1.48
0.50005	0.53407	6.580	0.51706	NTK	17.019	0.81
0.50024	0.53438	6.598	0.51731	NTK	17.258	2.23
0.60018	0.63423	5.517	0.61720	NTK	16.890	0.33
0.65002	0.68404	5.100	0.66703	NTK	16.713	-0.59
0.70022	0.70825	1.140	0.70423	T	17.285	2.92
0.70022	0.71290	1.796	0.70656	T	17.172	2.25
0.70067	0.71542	2.083	0.70805	T	17.231	2.61
0.69996	0.73398	4.746	0.71697	NTK	16.695	-0.56
0.73659	0.74810	1.551	0.74234	C	16.441	-2.00
0.89849	0.93259	3.725	0.91554	NTK	16.868	1.03
1.00644	1.05811	5.005	1.03227	C	16.351	-1.75
1.00644	1.07661	6.738	1.04152	C	16.368	-1.63
1.50353	1.52671	1.529	1.51512	NTK	16.625	1.23
1.53330	1.61084	4.933	1.57207	C	16.001	-2.41
2.00025	2.04114	2.024	2.02070	NTK	16.177	-0.11
2.10987	2.12209	0.578	2.11598	T	16.470	1.97
2.07848	2.15422	3.579	2.11635	C	15.822	-2.04
2.48067	2.49523	0.585	2.48795	NTK	16.316	2.08
2.51230	2.57375	2.417	2.54302	C	15.585	-2.35
2.99835	3.02128	0.762	3.00981	NTK	15.544	-1.31
3.04224	3.10808	2.141	3.07516	C	15.298	-2.69
3.47108	3.48569	0.420	3.47839	NTK	15.885	2.21
3.95386	3.97676	0.578	3.96531	NTK	15.538	1.39
4.00296	4.01998	0.424	4.01147	T	15.348	0.29
4.02538	4.09312	1.669	4.05925	C	14.893	-2.55
4.49490	4.51803	0.513	4.50646	NTK	15.352	1.78
4.96989	5.04408	1.482	5.00699	C	14.664	-1.33
5.48684	5.50970	0.416	5.49827	NTK	15.114	3.20
5.51129	5.67443	2.917	5.59286	T	14.887	1.94
6.00013	6.04098	0.679	6.02055	NTK	14.599	1.28
6.02826	6.09270	1.063	6.06048	C	14.275	-0.84
6.51222	6.59672	1.289	6.55447	C	14.087	-0.64
6.62707	6.69712	1.051	6.66210	NTK	14.000	-0.92
6.76277	6.83106	1.005	6.79691	C	14.026	-0.32

TABLE 2 (continued)

mol NH ₄ Br/1 kg H ₂ O		Relative concentration change (%)	Mean concentration	Type of calor.	-ΔH (kJ mol ⁻¹)	Δr
Initial m ₁	Final m ₂					
7.00649	7.05077	0.630	7.02863	NTK	13.900	-0.49
7.05301	7.14471	1.292	7.09886	C	13.917	-0.15
7.15327	7.19040	0.518	7.17184	T	13.950	0.32
7.28093	7.33579	0.751	7.30836	C	13.792	-0.38
7.56933	7.66242	1.222	7.61587	C	13.699	-0.08
7.71564	7.76045	0.579	7.73805	C	13.595	-0.45
7.84381	7.90197	0.739	7.87289	C	13.585	-0.09

aqueous solutions of NH₄Br to oversaturate, we prefer the lowest value given by Broul et al. [13], $m_s = 7.968$ mol NH₄Br/1 kg H₂O at 298.15 K.

Our pseudo-differential data, measured over the concentration range

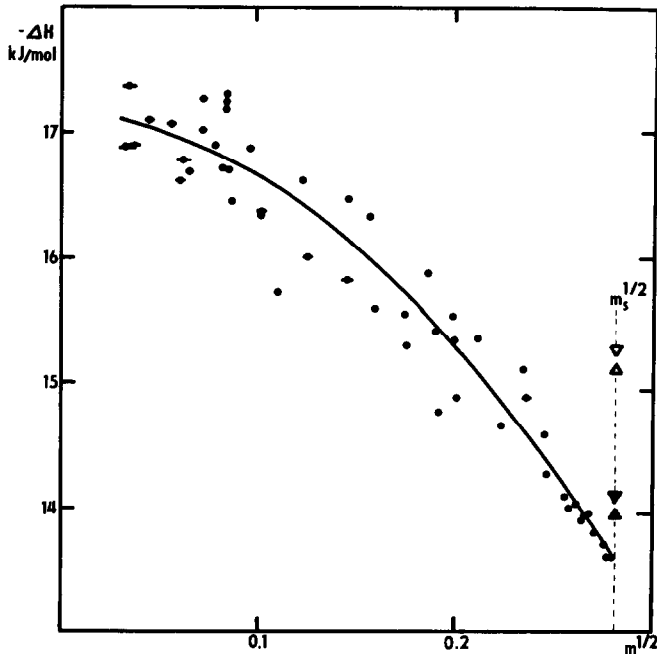


Fig. 2. Concentration dependence of the enthalpy of dissolution of ammonium bromide in water over a wide concentration range at 298.15 K. The bars on the points indicate the concentration changes in the experiments. (—) Regression parabola according to eqn. (2); m , molality (mol NH₄Br/1 kg H₂O); m_s , saturation molality at 298.15 K; $-\Delta H$, dissolution enthalpy in kJ mol⁻¹; (▷ ◁) uncertainty limits for the data of Voznesenskaya [11]; (▶ ◀) uncertainty limits for the data of Covington and Irish [12].

TABLE 3

Saturation concentration of ammonium bromide in water at 298.15 K

Authors:	Broul et al. [13]	Stephen et al. [14]	Voznesenskaya [11]	Smith et al. [15]	Scott et al. [16]
Saturation concentration (mol NH ₄ Br/ 1 kg H ₂ O)	7.968	8.12	7.98	8.097	7.977
$-(d \ln m_s)/d(1/T)$	866	857.2	—	863.2	—

6.25–7.84 mol NH₄Br/1 kg H₂O, were least-square fitted to give

$$-\Delta H = 19.3889 - 2.0654m^{1/2} \quad (3)$$

which is shown in Fig. 3.

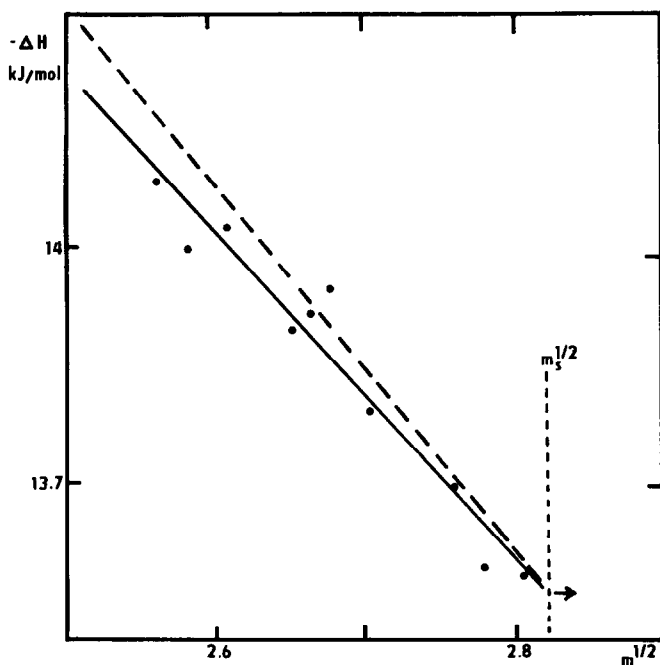


Fig. 3. Concentration dependence of the pseudodifferential enthalpy of dissolution of ammonium bromide in water at 298.15 K in the region approaching the saturation concentration. (●) Measured pseudodifferential enthalpies of dissolution with a maximum concentration change of 2%; (—) straight line obtained by eqn. (3); (- - - -) straight line obtained from all experimental data over the concentration range 6.25–7.84 mol NH₄Br/1 kg H₂O; m , molality (mol NH₄Br/1 kg H₂O); m_s , saturation concentration at 298.15 K; ΔH , differential enthalpy of dissolution in kJ mol⁻¹.

The last differential enthalpy of dissolution, which is equal in absolute value to the enthalpy of crystallization, was obtained from eqn. (3) by extrapolation to the saturation concentration of 7.968 mol NH₄Br/1 kg H₂O: $-\Delta H_{\text{cryst}} = \Delta H_{m_s} = -13.559 \text{ kJ mol}^{-1}$. Fitting all the values measured over the given concentration range to a straight line and extrapolating to the saturation concentration, we obtained an enthalpy of crystallization of 13.555 kJ mol⁻¹. Apparently, these values are the most precise results determined in this work. In view of a small uncertainty in the saturation concentration, we give the enthalpy of crystallization as $\Delta H_{\text{cryst}} = 13.55 \pm 0.05 \text{ kJ mol}^{-1}$.

Our data are most scattered in the region of dilute solutions, particularly within the molality range 0.7–1 m. It should be noted that, when applied to measurements of the enthalpy of dissolution of other salts, the same experimental method provided very much less scattered data compared with the present work [17–20]. We have no satisfactory explanation for this discrepancy. However, even though the maximum difference between our values for $m^{1/2} \approx 0.84\text{--}0.86$ is about 0.8 kJ mol⁻¹, it is still smaller than the uncertainty in the value of the first enthalpy of dissolution recommended by Parker [1].

The enthalpy of crystallization may also be evaluated from published data on the solubility [13–17] and the osmotic (ϕ) or activity (γ_{\pm}) coefficient [21–22] for NH₄Br–H₂O solutions:

$$\begin{aligned} \Delta H_{\text{cryst}} &= -\Delta H_{m_s} = -R \frac{d \ln m_s}{d(1/T)} \nu \left[\phi + \frac{d\phi}{d \ln m} \right]_{m_s, P, T} \\ &= -R \frac{d \ln m_s}{d(1/T)} \nu \left[1 + \frac{d \ln \gamma_{\pm}}{d \ln m} \right]_{P, T, m_s} \end{aligned} \quad (4)$$

where R is the gas constant (8.3144 J mol⁻¹ K⁻¹), and ν is the stoichiometric number of ions in a molecule of the salt ($\nu = 2$ for NH₄Br).

As seen from Table 3, there are only slight differences between the slopes of the solubility–temperature plot, $-(d \ln m_s)/d(1/T)$, given by various authors. The osmotic (ϕ) and activity (γ_{\pm}) coefficients published by Covington and Irish [12], Shults and Shimanova [23], and Voznesenskaya [11] are summarized in Table 4.

The value of the term $\nu[\phi(m_s) + (d\phi/d \ln m)_{m_s}]$ calculated from the osmotic coefficients reported by Covington and Irish [12] is 1.958, while the data of Voznesenskaya [11] give 2.12. The relative difference of ca. 1% between the maximum and minimum values of the temperature slope of solubility in Table 3 is very small (-857.2 [14]; -866 [13]), particularly when compared with the difference of about 8% between the values of the expression $\nu[\phi(m_s) + (d\phi/d \ln m)_{m_s}]$, a term which is a measure of the non-ideality of a solution at saturation. The last enthalpy of dissolution can be evaluated from both the values of the non-ideality term and the slope $-d \ln m_s/d(1/T)$ by means of eqn. (4).

TABLE 4

Published data of activity and osmotic coefficients of ammonium bromide

<i>m</i> (mol NH ₄ Br/1 kg H ₂ O)	Activity coefficients			Osmotic coefficients	
	[12]	[23]	[11]	[12]	[11]
5.0	0.591	0.595	0.575	0.975	0.973
5.5	0.592	0.597	0.576	0.980	0.979
6.0	0.594	0.598	0.578	0.985	0.985
6.5	0.595	0.598	–	0.988	–
7.0	0.596	0.600	0.582	0.991	0.992
7.5	0.596	0.601	–	0.994 *	–
7.765	–	–	–	0.9947 *	–
7.98	–	–	0.586	0.9952 ^a	1.000

^a Obtained by linear extrapolation of the data labelled *.

Using the data of Covington and Irish [12], we obtain an enthalpy of crystallization of 13.95 or 14.10 kJ mol⁻¹, while the data of Voznesenskaya [11] yield 15.11 or 15.25 kJ mol⁻¹. In Fig. 2, these values can be compared with those evaluated from our experimental data by means of eqns. (2) and (3). Clearly, the values of $\phi(m_s)$ and $d\phi/dm|_{m_s}$ published by Covington and Irish [12] are acceptably consistent with our value of $\Delta H(m_s)$, the relative difference being only about 3%. For the data of Voznesenskaya [11], on the other hand, the difference is larger, reaching nearly 12%.

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