

## Enthalpy of solution of ammonium iodide in water

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New molar enthalpies of solution of  $\text{NH}_4\text{I}$  in water at 298.15 K were measured in an LKB calorimeter. So as to prevent decomposition of ammonium iodide, hydroxylamine sulfate and sodium hydroxide were added in two different quantities. The molar enthalpies of solution extrapolated to infinite dilution are:  $(13877 \pm 37) \text{ J} \cdot \text{mol}^{-1}$  and  $(13871 \pm 41) \text{ J} \cdot \text{mol}^{-1}$ . In the absence of hydroxylamine sulfate and sodium hydroxide, values of  $(13940 \pm 35) \text{ J} \cdot \text{mol}^{-1}$  (Alfa) and  $(13983 \pm 12) \text{ J} \cdot \text{mol}^{-1}$  (Merck) were obtained.

### 1. Introduction

There is no reliable enthalpy of solution of  $\text{NH}_4\text{I}$  in water. The apparent reason for this lack is the rapid decomposition of  $\text{NH}_4\text{I}$  in water, seen by the appearance of a red color. In this work, the enthalpies of solution of  $\text{NH}_4\text{I}$  in water at 298.15 K are reported for samples from four different preparations. So as to prevent the oxidation of  $\text{NH}_4\text{I}$ ,  $\text{NH}_2\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  were added to the solid in an amount estimated to be 0.01 per cent by mass.<sup>(1)</sup> The crystals and aqueous solutions prepared in this way were found to remain free of any red color. Variations of this method of working with  $\text{NH}_4\text{I}$  have been employed previously in the preparation of  $\text{NH}_4\text{I}$  crystals,<sup>(1)</sup> and in the study of the equilibrium between  $(\text{NH}_4\text{I} + \text{KI})$  in aqueous and solid solutions.<sup>(2)</sup> As a check of the effect of the  $\text{NH}_2\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  addition on the measured enthalpy of solution, a set of measurements was performed in which the samples were prepared by using twice the amount of  $\text{NH}_2\text{H}_2\text{SO}_4$  and  $\text{NaOH}$ . Two sets of experiments were also performed with samples of  $\text{NH}_4\text{I}$  as obtained from commercial suppliers. The calorimetric procedure used here has been tested by measuring the molar enthalpy of solution of three samples of  $\text{KCl}$  from Alfa, Merck, and the NBS. The Merck sample was measured by two different operators.

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## 2. Experimental

### SAMPLE PREPARATION

Approximately 0.25 g of  $\text{NH}_2\text{H}_2\text{SO}_4$  and 0.12 g of NaOH were added to 200  $\text{cm}^3$  of boiling doubly distilled water.  $\text{NH}_4\text{I}$  from the freshly opened reagent bottle was added in sufficient quantity to prepare a solution whose concentration approximately corresponded to that of a saturated solution at 353 K. The  $\text{NH}_4\text{I}$  was Riedel-de Haen catalog number 03101, labelled chemically pure. Heating was continued until all of the solid dissolved. This solution at 353 K had a faint yellow tint. This solution was placed into a bath at around 273 K to precipitate the solid. The solution and precipitate at this temperature and in all subsequent manipulations were white.

The solid was collected on a fritted-glass suction filter. The crystals were then patted dry several times between layers of filter paper. The filtrate was placed in an oven at 383 K for 20 h. It was then removed, gently crushed with an agate mortar and pestle, and then returned to the oven for another 3 h. This is referred to as sample set A.

A sample returned to the oven was found to lose 0.005 mass per cent after 18 h at 383 K and a further 0.003 after an additional 24 h.

A second set of samples was prepared in an analogous manner except that approximately double the amounts of  $\text{NH}_2\text{H}_2\text{SO}_4$  and of NaOH were employed. This is referred to as sample set B.

Two sets of experiments were performed without addition of  $\text{NH}_2\text{H}_2\text{SO}_4$  and NaOH.  $\text{NH}_4\text{I}$  from Alfa Chemicals (catalog number 300920) and Merck (catalog number 1173) were each gently crushed and then dried for 2 d at 393 K. In contrast to the untreated Riedel-de Haen  $\text{NH}_4\text{I}$  for which a red color appears during the solution process, the solutions resulting from samples from Alfa and Merck remained free of any red color during the time required to complete each experiment.

So as to test for absence of calorimetric bias, potassium chloride from three separate sources was employed, as follows: Merck cat. No. 4933; Alfa Inorganics, Ultrapure, cat. No. 87626; U.S. National Bureau of Standards Reference Material 918. Each sample was gently crushed and then dried for 5 h at 773 K.

All of the ampoules were filled in the air immediately upon cooling of the sample after removal from the oven. The calorimetric system and procedure were essentially the same as previously reported.<sup>(3)</sup>

In spite of the correction for the enthalpy of evaporation of water to fill the air space in the ampoule being very small, it was erroneously taken in our last work<sup>(3)</sup> as 0.0531  $\text{J}\cdot\text{cm}^3$ . This value relates to the energy of evaporation instead of the enthalpy of evaporation, which should be 0.0561  $\text{J}\cdot\text{cm}^{-3}$ .<sup>(4)</sup> So as to keep our present results consistent with our previous ones, we make the assumption that 5 per cent less water vapor is absorbed into the air space. This is acceptable because the fraction of the escaping air from the ampoule which is actually saturated with water vapor during the main period of the experiment is not known.<sup>(5)</sup>

The molar masses  $M$  and the densities  $\rho$  used throughout this study are as

follows: KCl,  $M = 74.5513 \text{ g} \cdot \text{mol}^{-1}$ ,  $\rho = 1.988 \text{ g} \cdot \text{cm}^{-3}$ ;  $\text{NH}_4\text{I}$ ,  $M = 144.943 \text{ g} \cdot \text{mol}^{-1}$ ,  $\rho = 2.514 \text{ g} \cdot \text{cm}^{-3}$ .

### 3. Results and discussion

The results obtained for KCl and  $\text{NH}_4\text{I}$  are shown in tables 1 and 2, respectively.  $\Delta H$  is the enthalpy change in the experiment at  $\langle T \rangle$ , the average of the initial and final temperatures of the solution experiment;  $\Delta H(298.15 \text{ K})$  is the molar enthalpy of solution of the solute, after corrections for sample impurities in the case of Merck KCl, enthalpy of vaporization of water into the air space in the ampoule, and adjusted to 298.15 K. These adjustments were carried out as described previously.<sup>(3)</sup>  $\Delta H^\infty(298.15 \text{ K})$  is the enthalpy of solution calculated to conditions of infinite dilution.<sup>(5)</sup>

TABLE 1. Calorimetric results for enthalpies of solution of KCl

Run	$m_s$ g	$m$ mol · kg <sup>-1</sup>	$\Delta H$ J	$\langle T \rangle$ K	$\Delta H(298.15 \text{ K})$ J · mol <sup>-1</sup>	$\Delta H' (298.15 \text{ K})$ J · mol <sup>-1</sup>
KCl (Alfa, operator A)						
1	0.44956	0.06054	105.632	298.19	17517	17216
2	0.45036	0.06065	105.676	298.21	17496	17195
3	0.51825	0.06979	121.610	298.20	17496	17186
4	0.53087	0.07149	124.837	298.21	17535	17221
5	0.59119	0.07961	138.962	298.22	17530	17208
6	0.59377	0.07996	139.037	298.22	17463	17140
7	0.61511	0.08283	144.306	298.23	17498	17171
					17191 ± 21 <sup>a</sup>	
KCl (Merck, operator A)						
1	0.60053	0.08087	140.957	298.10	17498	17176
2	0.62315	0.08391	146.592	298.22	17557	17230
3	0.63126	0.08501	148.218	298.21	17522	17196
4	0.64919	0.08742	152.004	298.06	17499	17172
					17194 ± 26 <sup>a</sup>	
KCl (Merck, operator B)						
1	0.57286	0.07714	134.729	298.25	17557	17239
2	0.60511	0.08148	142.223	298.22	17541	17219
3	0.62105	0.08363	146.119	298.25	17564	17238
4	0.64016	0.08620	150.060	298.22	17495	17168
5	0.72509	0.09764	170.617	298.24	17565	17231
					17219 ± 26 <sup>a</sup>	
KCl (NBS, operator B)						
1	0.56942	0.07668	134.029	298.26	17560	17242
2	0.58946	0.07938	138.175	298.20	17479	17157
3	0.63106	0.08498	148.409	298.27	17547	17221
4	0.65524	0.08824	154.258	298.20	17555	17228
5	0.95350	0.12840	224.611	298.33	17588	17237
					17217 ± 31 <sup>a</sup>	

<sup>a</sup> Twice the standard deviation of the mean.

TABLE 2. Calorimetric results for enthalpies of solution of  $\text{NH}_4\text{I}$ 

Run	$m_s$ g	$m$ $\text{mol} \cdot \text{kg}^{-1}$	$\Delta H$ J	$\langle T \rangle$ K	$\Delta H(298.15 \text{ K})$ $\text{J} \cdot \text{mol}^{-1}$	$\Delta H^a(298.15 \text{ K})$ $\text{J} \cdot \text{mol}^{-1}$
$\text{NH}_4\text{I}$ , set A						
1	0.58677	0.04064	57.274	298.14	14136	13885
2	0.62457	0.04326	61.183	298.15	14189	13934
3	0.63956	0.04430	62.707	298.15	14202	13947
4	0.67232	0.04657	65.426	298.17	14099	13839
5	0.68690	0.04758	66.834	298.15	14095	13835
6	0.69145	0.04789	67.408	298.15	14122	13859
7	0.74200	0.05139	72.031	298.17	14066	13798
						$13871 \pm 41^a$
$\text{NH}_4\text{I}$ , set B						
1	0.59709	0.04136	58.109	298.14	14095	13844
2	0.60190	0.04169	58.745	298.14	14135	13880
3	0.61903	0.04288	60.390	298.14	14129	13874
4	0.63331	0.04386	61.515	298.14	14068	13813
5	0.63821	0.04420	62.499	298.07	14174	13918
6	0.71773	0.04971	70.340	298.15	14197	13934
						$13877 \pm 37^a$
$\text{NH}_4\text{I}$ (Alfa)						
1	0.55342	0.03833	54.299	298.13	14207	13960
2	0.61086	0.04231	60.031	298.17	14237	13981
3	0.67496	0.04675	66.043	298.21	14182	13923
4	0.72330	0.05010	70.944	298.24	14221	13956
5	0.74923	0.05189	73.650	298.17	14243	13971
6	0.75872	0.05255	74.465	298.15	14218	13946
7	0.76162	0.05275	74.809	298.14	14228	13956
8	0.78253	0.05420	76.134	298.18	14099	13823
						$13940 \pm 35^a$
$\text{NH}_4\text{I}$ (Merck)						
1	0.63513	0.04399	62.507	298.14	14254	13995
2	0.63540	0.04401	62.406	298.13	14224	13968
3	0.68480	0.04743	67.319	298.14	14239	13979
4	0.68966	0.04777	67.819	298.21	14254	13991
						$13983 \pm 12^a$

<sup>a</sup> Twice the standard deviation of the mean.

Literature values of  $C_{\phi, m}^{(6)}$ ,  $C_{p, m}^{(7)}$  and of  $\Delta_{\text{dil}}H^{(6)}$  were employed. The values<sup>(6)</sup> relating to aqueous  $\text{NH}_4\text{I}$  solutions were estimated.

The analysis of KCl samples was performed as a check against calorimetric bias in our measurements. The results obtained were adjusted to the standard test-reaction conditions as recommended by IUPAC<sup>(8)</sup> and are as follows:  $\text{KCl(c)} + 200\text{H}_2\text{O(l)} = \text{KCl} \cdot 200\text{H}_2\text{O(l)}$ ;  $\Delta H(298.15 \text{ K})/(\text{J} \cdot \text{mol}^{-1}) = (\text{recommended IUPAC value}) (17550 \pm 40)$ ; (Alfa)  $(17530 \pm 21)$ ; (Merck, Operator A)  $(17533 \pm 26)$ ; (Merck, Operator B)  $(17558 \pm 26)$ ; (NBS RM 918)  $(17556 \pm 31)$ , the uncertainties in our measurements being twice the standard deviation of the mean.



on of  $\text{NH}_4\text{I}$ 

$H(298.15 \text{ K})$ $\text{J} \cdot \text{mol}^{-1}$	$\Delta H^\circ(298.15 \text{ K})$ $\text{J} \cdot \text{mol}^{-1}$
14136	13885
14189	13934
14202	13947
14099	13839
14095	13835
14122	13859
14066	13798
	$13871 \pm 41^a$
14095	13844
14135	13880
14129	13874
14068	13813
14174	13918
14197	13934
	$13877 \pm 37^a$
14207	13960
14237	13981
14182	13923
14221	13956
14243	13971
14218	13946
14228	13956
14099	13823
	$13940 \pm 35^a$
14254	13995
14224	13968
14239	13979
14254	13991
	$13983 \pm 12^a$

The values obtained are within the limits of error for the value recommended by IUPAC.

The values obtained for our  $\text{NH}_4\text{I}$  sets A and B, corresponding to two different quantities of the additives, are in agreement with one another. Thus, in the concentration range of  $\text{NH}_2\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  studied, there is no effect on the enthalpy of solution of ammonium iodide.

The  $\text{NH}_4\text{I}$  samples obtained from Alfa and Merck were in excellent condition without visible evidence of decomposition, in contrast to the Riedel-de Haen sample. Therefore it is not surprising that both sets, with and without additives, yield enthalpies of solution that are so close to each other.

Because no modern investigation of comparable accuracy exists for  $\text{NH}_4\text{I}$  in the literature, these values can be taken as the "best values".

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employed. The values<sup>(6)</sup>

against calorimetric bias  
d to the standard test-  
and are as follows:  
( $\text{J} \cdot \text{mol}^{-1}$ ) = (recom-  
: (Merck, Operator A)  
1918) ( $17556 \pm 31$ ), the  
deviation of the mean.