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STANDARD ENTHALPY OF SOLUTION OF AMMONIUM NITRATE IN WATER AT 298 K

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ABSTRACT

We have made calorimetric measurements of the enthalpy of solution of NH_4NO_3(c, IV) in water at 298 K, where (c, IV) indicates the crystal form of ammonium nitrate that is stable from 256 to 305 K. Results of our measurements have been combined with enthalpy of dilution values from Parker to obtain the standard enthalpy of solution of NH_4NO_3 (c, IV) in water at 298.15 K to be $\Delta H^0 = 25.41$ kJ mol^{-1}.

INTRODUCTION

Several thermochemical cycles have been considered[1] in NBS Tech. Note 270-3[2] and are being considered[1] by the CODATA Task Group on Key Values for Thermodynamics in connection with ΔH_f° values for NH_4^+(aq), NO_3^-(aq), NH_4NO_3(c, IV), and various related species such as HNO_3(g). Among new measurements required to resolve remaining uncertainties and discrepancies in these important quantities is the enthalpy of solution of NH_4NO_3(c, IV).

Parker[3] has reviewed a number of calorimetric investigations of the enthalpy of solution of ammonium nitrate that were carried out between 1853 and 1937 at temperatures from 16 to 28°C. On the basis of these results and auxiliary quantities (heat capacities and enthalpies of dilution), she has calculated standard enthalpies of solution at 298 K ranging from 5990 to 6216 cal mol^{-1} (25.06 to 26.01 kJ mol^{-1}) and has selected $\Delta H^0 = 6140 \pm 50$ cal mol^{-1} (25.69 $\pm$ 0.21 kJ mol^{-1}) as the "best" standard enthalpy of solution at 298 K. This choice is consistent with the ΔH_f° values listed by Parker and others[2] in NBS Tech. Note 270-3.

Parker's[3] "best" ΔH^0 value cited above is intended to refer to the standard enthalpy of solution of NH_4NO_3(c, IV), where (c, IV) indicates the crystal form that is stable from 256 to 305 K. Steiner and Johnston[4] have noted that the transition at 305 K between the forms denoted by (c, IV) and (c, III) is slow; it is therefore reason-

able to wonder whether calorimetric measurements in the temperature range 16 to 28°C were actually made on the stable (c, IV) or possibly on mixtures of this form with the higher temperature form (c, III). Because Stephenson et al.[5] have found that $\Delta H = 409.9$ cal mol^{-1} (1715 J mol^{-1}) for the transition (c, IV) = (c, III), uncertainties about crystal forms used by various investigators are significant. Because of uncertainties associated with crystal forms and because the measurements cited by Parker[3] were made more than 40 years ago at temperatures other than 25°C, we have undertaken the measurements described in this paper.

EXPERIMENTAL

All calorimetric measurements in both Moscow and Lethbridge have been made with the LKB 8700 precision calorimetry system. Standard LKB 100-ml glass reaction calorimeters were used with 1-ml glass ampoules to contain solids to be dissolved. Several calorimetric runs were made in each laboratory with air-filled ampoules to establish the small heat of ampoule breaking. Calibration constants for all runs were evaluated as the mean of two electrical calibrations, one before and one after the sample was dissolved.

The thermistors of both calorimeters were calibrated against quartz crystal thermometers that had been standardized previously at the triple point of water. These calibrations were accurate to 0.005°C and final enthalpies of solution refer to 25.00 ± 0.01°C.

A commercial sample of chemically pure NH_4NO_3 obtained in Moscow was recrystallized three times from doubly distilled water. This purified material was used to prepare a saturated solution in doubly distilled water at a temperature slightly lower than 30°C. The solution was then stored at room temperature for several days, during which time water slowly evaporated and crystals of ammonium nitrate were precipitated. These crystals were separated from solution, dried in a desiccator above P_2O_5, ground in an agate mortar, and again dried in a desiccator above P_2O_5 to constant mass. X-ray analysis of the samples prepared in this manner showed the crystal structure[6] of the rhombic form we designate (c, IV). Here we note that ammonium nitrate samples obtained by precipitation from solution at a temperature above 30°C gave a mixture of (c, IV) and (c, III).

Starting material for all measurements made in Lethbridge was Certified A.C.S. NH_4NO_3 from Fisher Chemical Company. Sample A was prepared from this material by heating at 110°C for 24 h and then storing at room temperature for three days before measurements were made. Sample B was prepared by heating at 110°C for 70 h and then storing for three days at room temperature. Sample C was transferred from the original bottle to a desiccator containing P_2O_5 (all at room temperature) and stored for six days before measurements were made, while sample D was stored with P_2O_5 for 21 days before calorimetric measurements were made. Finally, sample E was prepared by making a saturated solution in distilled water at 28°C. This solution was decanted from the crystals in the bottom of the flask and cooled slowly to 0°C

with frequent stirring. The resulting crystals were collected on a sintered glass filter and transferred to two dishes in a desiccator containing P_2O_5. Each day for two months the crystals were moved around in their dishes and lumps were *gently* broken up with a glass rod. After sixty days, it was found that the mass of a test sample did not decrease detectably on further storage in the desiccator for 10 days. Prolonged heating of test samples at 100°C led to mass loss less than 0.2%.

It was observed in preliminary experiments that the weights of samples in Moscow increased while exposed to air. A glove box with dry N_2 was therefore used for transferring samples to calorimetric ampoules. Masses of samples were calculated by taking into account the effect of buoyancy, including the effect of having nitrogen (instead of air) in the ampoules. Masses of samples are judged to be accurate to 5×10^{-5} g.

Presumably, because of the relatively low humidity in Lethbridge and the somewhat larger crystals used, no weight change was observed during brief exposure to air while weighing. Buoyancy corrections were made in the usual way. Some samples were weighed to 10^{-4} g with an "ordinary" balance, while others were weighed to 10^{-6} g with a microbalance.

We have used 80.043_5 g mol^{-1} as the molecular weight of NH_4NO_3.

RESULTS

Results of all our calorimetric measurements are summarized in Tables 1 and 2. All of these results refer to 298.15 K. To obtain these values that refer to 298.15 K, it was necessary to make small ΔC_p corrections based on heat capacities of NH_4NO_3(c) and NH_4NO_3(aq) from Stephenson et al.[5] and from Singh and Hepler[7], respectively. The largest of these corrections amounted to only 0.010 kJ mol^{-1}. Enthalpies of

TABLE 1

ENTHALPIES OF SOLUTION OF NH_4NO_3(c) AT 298.15 K AS DETERMINED IN MOSCOW

Mass NH_4NO_3(g)	*ΔH (kJ mol^{-1})*	*ΔH° (kJ mol^{-1})*
0.45713	25.613	25.391
0.39054	25.674	25.457
0.42831	25.837	25.617*
0.37243	25.555	25.340
0.48774	25.643	25.421
0.59810	25.571	25.351
0.49270	25.672	25.450
0.46943	25.615	25.393
0.50055	25.611	25.389
0.51131	25.569	25.347
0.57079	25.606	25.385
0.51701	25.595	25.373

TABLE 2

ENTHALPIES OF SOLUTION OF $NH_4NO_3(c)$ AT 298.15 K AS DETERMINED IN LETHBRIDGE

Sample	*Mass $NH_4NO_3(g)$*	*ΔH (kJ mol^{-1})*	*ΔH^0 (kJ mol^{-1})*
A	0.1599	25.78	25.60
A	0.1082	25.79	25.63
A	0.1070	25.91	25.75
B	0.1122	25.77	25.61
B	0.2176	25.79	25.59
B	0.0722	25.57	25.43
B	0.1421	25.93	25.75
C	0.108924	25.631	25.468
C	0.118190	25.631	25.464
D	0.135166	25.777	25.601
D	0.136766	25.798	25.622
E	0.501364	25.669	25.447
E	0.508964	25.644	25.422
E	0.155582	25.560	25.376
E	0.267603	25.669	25.460
E	0.429052	25.666	25.444
E	0.439015	25.677	25.455
E	0.244502	25.627	25.422

dilution used to obtain standard state ΔH^0 values from our tabulated ΔH values have all been taken from Parker's tabulation[3].

The average (except for the result marked with *) of the ΔH^0 values based on measurements made in Moscow is $\Delta H^0 = 25.391$ kJ mol^{-1}, with standard deviation 0.039 kJ mol^{-1}. This value is significantly smaller (0.30 kJ mol^{-1}) than the value selected by Parker[3] from results of earlier measurements.

The average of all of the ΔH^0 values based on measurements made in Lethbridge is $\Delta H^0 = 25.53$ kJ mol^{-1} with standard deviation 0.12 kJ mol^{-1}. We note, however, that there appears to be a significant difference between the Lethbridge results for sample E and for all other samples. We therefore also use these results to find that the average of all results for samples A–D is $\Delta H^0 = 25.59$ kJ mol^{-1} with standard deviation 0.10 kJ mol^{-1}, while the average of all results for sample E is $\Delta H^0 = 25.432$ kJ mol^{-1} with standard deviation 0.029 kJ mol^{-1}. All of these average ΔH^0 values are smaller than the value selected by Parker[3] on the basis of earlier experiments; the value based only on sample E is in excellent agreement with the average ΔH^0 value from measurements made in Moscow.

Because of the impressive agreement of $\Delta H^0 = 25.391$ kJ mol^{-1} from Moscow with $\Delta H^0 = 25.432$ kJ mol^{-1} for sample E from Lethbridge, we choose $\Delta H^0 = 25.41$ kJ mol^{-1} as the "best" standard enthalpy of solution of NH_4NO_3(c, IV) at 298.15 and estimate that the *total* uncertainty (due to our calorimetry, enthalpies of dilution, chemical problems) is less than twice the standard deviation (0.040 kJ mol^{-1}) calculated for eleven results from Moscow and seven results from Lethbridge.

Before undertaking the investigations reported here, it seemed to us that the most likely source of error associated with the measurements made in Lethbridge on samples A–D would be contamination of the desired NH_4NO_3(c, IV) with uncertain amounts of the high temperature form represented by NH_4NO_3(c, III). On the basis of this expectation in combination with our "best" $\Delta H^0 = 25.41$ kJ mol^{-1} selected above and $\Delta H^0 = 1.72$ kJ mol^{-1} for transformation of (c, IV) to (c, III), we obtain

$$\Delta H^0 = 25.41 - 1.72f$$

in which f represents the fraction of (c, III) as the standard enthalpy of solution of a mixture. This approach leads us to expect that enthalpies of solution of (c, IV) mixed with (c, III) would be *smaller* than the enthalpy of solution of pure (c, IV), rather than *larger* as observed for samples A–D.

Because the considerations above are unable to account for the "too large" results obtained for samples A–D, we should consider the possibility that these results for samples A–D are the "best" values and that all results obtained in Moscow and those for sample E obtained in Lethbridge are too low for some reason. We consider that the most likely source of "too low" results on the Moscow sample and sample E in Lethbridge would be from water that was not removed. However, we reject this as a significant error for several reasons. First, in both Moscow and Lethbridge we have shown that our stored samples attained (apparent) constant mass. If any water remained in or on these crystals, the excellent agreement of calorimetric results for the Moscow material and sample E in Lethbridge can only be explained on the basis that both samples (handled in different ways) contain the same amount of impurity, which does not seem likely. Second, it was shown in Lethbridge that prolonged heating led to a maximum weight loss of less than 0.2%. Making the pessimistic assumption that the Moscow sample and sample E in Lethbridge contained 0.2% water, we calculate that the corresponding ΔH^0 would be too small by 0.05 kJ mol^{-1}, which can account for only one-fourth of the discrepancy between our selected "best" value and the larger ΔH^0 for samples A–D in Lethbridge.

Although we are unable to explain the "too large" results reviewed by Parker[3] or obtained with samples A–D in Lethbridge, the considerations above lead us to return to our selection of $\Delta H^0 = 25.41$ kJ mol^{-1} as the "best" available standard enthalpy of solution of NH_4NO_3(c, IV) at 298.15 K.

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