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RECEIVED for review July 24, 1967. Accepted November 6, 1967.

# Heat of Solution of Ammonium Bromide and the Entropies of the Aqueous $NH_4^+$ and $Br^-$ Ions

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**The heat of solution of $NH_4Br$ has been determined as 4007 ± 15 cal. per mole. This datum has been combined with literature data to calculate the partial molal entropies of the aqueous ammonium and bromide ions as 26.6 ± 0.1 and 19.8 ± 0.1 cal. per (mole °K.), respectively. A thermochemical path has been devised to calculate $\Delta H^\circ$ = 45.18 kcal. per mole for the reaction $NH_4Br(c) = NH_3(g) + HBr(g)$, in good agreement with a value derived from dissociation pressures.**

THIS study was undertaken to provide a value for the heat of solution of $NH_4Br$—useful in the correlation of literature data concerning this material and related substances. Thermochemical paths were devised by which this heat of solution could be used to: confirm values for the partial molal entropies of the aqueous ammonium and bromide ions; confirm high temperature dissociation pressures of $NH_4Br$; calculate the heat of solution of $NH_3$(g) in water; and determine an indirect value for the $Br_2$(liq)/Br (aq) electrode potential.

## EXPERIMENTAL

The calorimeter and its adjuvant electrical circuitry closely follow the design of Wu, Birky, and Hepler (*48*). The reaction chamber is a silvered glass Dewar of ca. 950-ml. capacity, tapered at the open end to seal against O-ring gaskets about its aluminum cover. The aluminum cover is suspended from the top plate of a brass submarine that encloses the calorimeter. The submarine is, in turn, suspended from the top plate of a ca. 50-gallon water bath. Three brass chimneys pass from the bath top plate to the submarine and are aligned over corresponding holes through the aluminum calorimeter cover. The chimneys are of sufficient length to ensure that the submarine lies completely beneath the water level of the 50-gallon bath. One of the chimneys contains the calorimeter stirrer, another the electrical leads, and the third the sample holding device.

The calorimeter fluid is stirred by a glass spiral that terminates in a four-bladed propellor. The stirrer is held fixed by two ball-bearing seals and is driven through a belt and pulley system by a R.M.S. SCPVBK motor. Within the calorimeter the stirrer lies along the axis of a cylinder formed by a glass tubing spiral. The spiral contains the bifilarly wound calorimeter heater (250 ohms of No. 38 Manganin wire) and is filled with paraffin oil to facilitate heat exchange between the heater and the calorimeter fluid.

Samples that are not sensitive to air are contained in thin-walled glass bulbs of ca. 15-ml. capacity. The bulbs are fitted to the end of a spring-loaded glass rod by a wax seal. The rod passes through the aluminum calorimeter cover and through one of the chimneys to the outside. The reaction is initiated by depressing the rod to crush the bulb against a reinforced section of the calorimeter bottom.

Temperatures are sensed by a multijunction (5 or 10) copper-constantan thermocouple fabricated from No. 28 or No. 30 wire. The thermocouple is contained in an oil-filled well extending into the calorimeter fluid. The reference junctions are maintained in an external slurry of distilled-water ice.

The 50-gallon water bath is maintained at a preselected temperature (usually 1.5° C. above the calorimeter temperature) by the compensating actions of a Sargent water bath cooler and a 750-watt immersion heater controlled by a Fisher proportional temperature control. Temperature uniformity is maintained to ±0.02° C. by an additional circulating pump.

The heat capacity of the calorimeter and its contents is determined separately for each experiment from the temperature rise caused by the passage of current through the Manganin heater. Power is supplied to the heater by a Kepco regulated d.c. power supply. The heater current is determined by monitoring the potential drop across a Leeds and Northrup 4025-B standard 10-ohm resistor. Typically a current of 80 ma. is passed through the heater for 2 minutes. The resistance of the heater is determined

### Table I. Sum of the Entropies of $NH_4^+$(aq) and $Br^-$(aq)

Units: cal. per (mole ° K.)

| $MX$ | $\bar{S}_2^\circ(NH_4X)$ + | $\bar{S}_2^\circ(MBr)$ − | $\bar{S}_2^\circ(MX)$ = | $\bar{S}_2^\circ(NH_4Br)$ |
|---|---|---|---|---|
| KCl | $40.2_2$ (*21, 41, 46*) | $44.0_0$ (*2, 9, 20*) | $37.6_4$ (*16, 24, 34*) | 46.6 |
| $KNO_3$ | $61.6_9$ (*24, 42*) | $44.0_0$ | $59.3_6$ (*18, 31, 39*) | 46.3 |
| ½$K_2SO_4$ | $28.7_5$ (*16, 33, 47*) | $44.0_0$ | 26.4 (*16, 22, 32*) | 46.4 |
| NaCl | $40.2_2$ | 33.9 (*3, 7, 24, 26, 43*) | $27.5_7$ (*16, 24, 30, 36*) | 46.5 |
| $NaNO_3$ | $61.6_9$ | 33.9 | $49.2_2$ (*16, 17, 25*) | 46.4 |
| ½$Na_2SO_4$ | $28.7_5$ | 33.9 | $16.2_2$ (*28, 32*) | 46.4 |
| AgCl | $40.2_2$ | $37.1_6$ (*8, 16, 23*) | $31.0_1$ (*6, 29*) | 46.4 |
| $AgNO_3$ | $61.6_9$ | $37.1_6$ | $52.5_9$ (*14, 16, 24*) | 46.3 |
| ½$Ag_2SO_4$ | $28.7_5$ | $37.1_6$ | $19.5_5$ (*10*) | 46.4 |

### Table II. Entropy Difference $[\bar{S}_2^\circ(Br^-) - \bar{S}_2^\circ(Cl^-)]$

Units: cal. per (mole ° K.)

| $M$ | $\bar{S}_2^\circ(MBr)$ − | $\bar{S}_2^\circ(MCl)$ = | $[\bar{S}_2^\circ(Br^-) - \bar{S}_2^\circ(Cl^-)]$ |
|---|---|---|---|
| $NH_4^+$ | $46.3_8$ | $40.2_2$ | 6.2 |
| $K^+$ | $44.0_0$ | $37.6_4$ | 6.4 |
| $Na^+$ | 33.9 | $27.5_7$ | 6.3 |
| $Ag^+$ | $37.1_6$ | $31.0_1$ | 6.2 |
| | Natl. Bur. Std. (*45*) | | 6.2 |

in a separate experiment by comparing the potential drops across it and a standard resistor in series with it. All measurements of electrical potential are made with a Leeds and Northrup guarded six-dial potentiometer and a Leeds and Northrup electronic null detector. Time intervals are determined with Standard timers.

The calibration and method of use of the calorimeter were tested by determining the heat of solution of KCl. Eight determinations using oven-dried Fisher certified reagent KCl and distilled water to give final concentrations in the range $m = 0.014$ to 0.084 were made at 25.0 ± 0.1° C. These data, corrected to standard state conditions with relative apparent molal enthalpies tabulated by the National Bureau of Standards (*24*), average at $\Delta H^\circ = 4118 \pm 10$ (r.m.s. deviation) cal. per mole. The latest "best" value selected by the National Bureau of Standards (*24*) is 4115 ± 10 cal. per mole.

The primary calorimetric sample was oven-dried Fisher certified reagent $NH_4Br$, the lot assay of which indicated a maximum of 0.3% chloride. Total halide content, by the Volhard method, led to a calculated purity of $99.8_1 \pm 0.1_0$% as based on $NH_4Br$. Thirteen determinations of the heat of solution of this material in distilled water ($m = 0.009$ to 0.055) were fitted to the least-squares straight line $\Delta H_{obsd} = (4005._2 \pm 8.0) + (413 \pm 47)m^{1/2}$ cal. per mole, where the uncertainties in slope and intercept are the probable errors (*19*).

A portion of the sample described above was recrystallized twice from distilled water and oven-dried under vacuum at 140° C. Halide analysis indicated a purity of $99.8_6 \pm 0.0_6$% on the basis of $NH_4Br$. Three determinations of the heat of solution of this material at $m = 0.012$, 0.018, and 0.038 were indistinguishable from the previous results within the estimated experimental uncertainty of ±15 cal. per mole. Both sets of data were fitted to the least-squares straight line $\Delta H_{obsd} = (4007._4 \pm 7._4) + (394 \pm 45)m^{1/2}$.

## PARTIAL MOLAL ENTROPIES OF THE AQUEOUS AMMONIUM AND BROMIDE IONS

Parker (*24*) has reviewed previous determinations of the heat of solution of $NH_4Br$, and has selected a "best" value of $\Delta H^\circ = 4010 \pm 100$ cal. per mole. From the present measurements, the authors choose $\Delta H^\circ = 4007 \pm 15$ cal. per mole. The agreement is fortuitous, since Parker's value is based largely on two discordant values—4064 ± 50 and 3920 ± 50 cal. per mole.

Shul'ts and Simanova (*35*) have recently reported the activity coefficients of $NH_4Br$ solutions. Their data and the solubility (*40*) lead to

$$NH_4Br(c) = NH_4^+(aq) + Br^-(aq) \qquad (1)$$

$$\Delta G_1^\circ = -RT \ln (0.603)^2 (8.12)^2 = -1883 \text{ cal. per mole}$$

From this value and the heat of solution, $\Delta S_1^\circ = (4007 + 1883)/298 = 19.7_6 \pm 0.1$ cal. per(mole ° K.). The third-law entropy of $NH_4Br$(c) has been determined by Cole (*5*) as 26.62 ± 0.1 cal. per (mole ° K.), leading to $\bar{S}_2^\circ = 19.7_6 + 26.62 = 46.4$ cal. per (mole ° K.) for $NH_4Br$(aq). A second value exists for the entropy of $NH_4Br$(c) based on heat capacity measurements (*38*) that are 1% higher than those of Cole. These values may be compared with $\Delta G_1^\circ = -1.8$ kcal. per mole and $\Delta S_1^\circ = 19._8$ cal. per (mole ° K.) from the latest NBS compilation (*45*).

The sum of the partial molal entropies of the aqueous ammonium and bromide ions can also be obtained by several other paths. For example, the heat of solution (*24*), free-energy of solution (*34*), and third-law entropy (*16*) for KCl(c) can be combined to give $\bar{S}_2^\circ = 37.6_4$ cal. per (mole ° K.) for KCl(aq). Similar data for KBr(c) (*2, 9, 20*) and $NH_4Cl$(c) (*21, 41, 46*) give $\bar{S}_2^\circ = 44.0_0$ and $\bar{S}_2^\circ = 40.2_2$ cal. per (mole ° K.) for KBr(aq) and $NH_4Cl$(aq), respectively. These calculations can be combined to give $\bar{S}_2^\circ(KBr) + \bar{S}_2^\circ(NH_4Cl) - \bar{S}_2^\circ(KCl) = \bar{S}_2^\circ(NH_4Br) = 44.0_0 + 40.2_2 - 37.6_4 = 46.6$ cal. per (mole ° K.) for the sum of the partial molal entropies of the aqueous ammonium

### Table III. Heat and Free Energy of Dissociation of $NH_4Br$

Units: cal. per (mole ° K.) at 298° K.

| | $\Delta G^\circ$ | $\Delta H^\circ$ | $\Delta S^\circ$ |
|---|---|---|---|
| $NH_4Br(c) = NH_4^+(aq) + Br^-(aq)$ | −1883 | 4007 | 19.8 |
| $H^+(aq) + Br^-(aq) = HBr(g)$ | 12100 | 20350 (*44*) | 27.7 |
| $NH_4OH(aq) = NH_3(g) + H_2O(liq)$ | 2410 (*45*) | | |
| $NH_4^+(aq) + OH^-(aq) = NH_4OH(aq)$ | −6480 (*45*) | −865 (*27*) | |
| $H_2O(liq) = H^+(aq) + OH^-(aq)$ | 19090 (*45*) | 13345 (*45*) | −19.3 |
| $NH_4Br(c) = NH_3(g) + HBr(g)$ | 25240 | 45180 | $66.8_8$ |

and bromide ions. Similar calculations involving other compounds have been summarized in Table I.

The accord shown by the entries in the last column in Table I is excellent, and 46.4 ± 0.1 cal. per (mole °K.) is adopted for the sum of the entropies of $NH_4^+$(aq) and $Br^-$(aq). Some of the data in Table I may also be used to derive the entropy difference between the aqueous bromide and chloride ions (Table II).

The average difference (Table II) is 6.3 ± 0.1 cal. per (mole °K.). Taking the entropy of $Cl^-$(aq) as 13.5 ± 0.1 cal. per (mole °K.) (*8*, *10*), $\bar{S}^\circ_2(Br^-) = 19.8 \pm 0.1$ cal. per (mole °K.) and $\bar{S}^\circ_2(NH_4^+) = 26.6 \pm 0.1$ cal. per (mole °K.). It is also possible to calculate partial molal entropies for other ions from the data presented in Tables I and II. The results are: $K^-$ (24.2), $Na^-$ (14.1), $Ag^-$ (17.5), $NO_3^-$ (35.1), $SO_4^{-2}$ (4.2)—all ±0.1 cal. per (mole °K.). These values may be compared with those of the latest NBS compilation (*45*) which are 24.5, 14.1, 17.40, 35.0, and 4.8 cal. per (mole °K.), respectively.

## HIGH TEMPERATURE DISSOCIATION OF $NH_4Br(c)$

Smits and Purcell (*37*) investigated the equilibrium

$$NH_4Br(c) = NH_3(g) + HBr\ (g) \qquad (2)$$

between 605° and 670° K. Cole (*5*), using extrapolated heat capacity data for $NH_4Br$ (assuming it to follow the heat capacity of $NH_4Cl$) and Bridgman's value for the heat of transition at 411° K. (*4*), calculated $\Delta H^\circ_2 = 45.15 \pm 0.15$ kcal. per mole at 298° K. More recent data for the heat of transition (*1*) and high temperature heat-contents (*15*) lead to the same value within the stated uncertainty. It is now possible to check this value by the following path.

The $\Delta H^\circ_2 = 45.18$ kcal. per mole (derived from $\Delta G^\circ_2$ and $\Delta S^\circ_2$ in Table III) agrees well with that calculated from the high temperature dissociation data by Cole (*5*). This $\Delta H^\circ_2$ may also be combined with the other $\Delta H^\circ$ values in Table III to give $\Delta H^\circ = -8.36$ kcal. per mole for the solution of $NH_3(g)$ in water, $NH_3(g) + H_2O(liq) = NH_4OH$(aq, unionized). Parker (*24*) mentions data that lead to $\Delta H^\circ$ values between −8.16 and −8.45 kcal. per mole.

## $Br_2$(LIQ)/$Br^-$(AQ) ELECTRODE POTENTIAL

In the revision of NBS Circular 500 (*45*) Wagman *et al.*, tabulate $\Delta H^\circ_f = -29.05$ kcal. per mole for $Br^-$(aq). This value is based, in part, on recent thermochemical data (*11*, *12*). This $\Delta H^\circ_f$ and the entropies of $Br_2$(liq) (*16*) and $Br^-$(aq) permit a calculation of $\Delta G^\circ_f = -29050 - 298(19.8 - 18.2 - 15.6) = -24.88$ kcal. per mole; and $E^\circ = 1.0788$ volts for the potential of $Br^-(aq) = \frac{1}{2} Br_2(liq) + e^-$. The experimental value (*13*) is −1.0652 volts corresponding to $\Delta G^\circ_f = -24.56$ kcal. per mole. Comparison of the two values indicates an error of about 300 cal. in the heat of formation or 0.013 volts in the electrode potential. Using the $G^\circ_f = -23.16$ kcal. per mole given in NBS 270-1 (*45*) the experimental electrode potential may be recalculated as −1.0755 volts. Until the National Bureau of Standards completes its tables and makes its references available, such a calculation may be a circular argument.

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RECEIVED for review August 18, 1967. Accepted November 9, 1967. Division of Physical Chemistry, 153rd Meeting, ACS, Miami, Fla., April 1967. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, who supported part of this research. The partial financial support of the National Aeronautics and Space Administration through sustaining Grant NGR-46-001-008 to the University of Vermont, and of the Research Corporation is also gratefully acknowledged.