

Enthalpies of solution of rubidium halides in water

ROBERT WEINTRAUB,^a ALEXANDER APELBLAT, and
ABRAHAM TAMIR

*Department of Chemical Engineering, Ben Gurion University of the Negev,
Beer Sheva, Israel*

(Received 10 December 1981; in revised form 4 March 1982)

Enthalpies of solution of different samples of RbCl and of RbBr and RbI in water at 298.15 K were measured. The values obtained extrapolated to infinite dilution are: RbCl (Alfa) (16975 ± 27) J·mol⁻¹, RbCl (Merck Suprapur) (16877 ± 46) J·mol⁻¹, RbCl (Merck) (16908 ± 27) J·mol⁻¹, RbBr (Alfa) (22184 ± 30) J·mol⁻¹, RbI (Alfa) (25597 ± 27) J·mol⁻¹.

1. Introduction

The many reported experimental studies of aqueous RbCl are summarized in the literature^(1,2) (see also references 3, 4, and 5). There exists a significant scatter among the reported experimental results. The existing results for RbBr⁽⁶⁾ and RbI^(6–8) are not within sufficient accuracy for use in many thermodynamic calculations. The aim of this work was to fill these gaps by presenting reliable values of high accuracy for the rubidium halides.

Measurements of the enthalpies of solution of RbCl, RbBr, and RbI in water at 298.15 K are reported. The calorimetric procedure has been tested by measuring the enthalpy of solution of two samples of KCl.

2. Experimental

MATERIALS

The salts measured in this study are described below: potassium chloride, Merck, Cat. No. 4933, *pro analysi*, assay of KCl ≥ 99.5 mass per cent; potassium chloride, Ultrapure, Alfa Inorganics, Cat. No. 87626 (ultrapure compounds from Alfa are reported as containing “exceptionally low levels of metallic impurities”); rubidium chloride, Merck, Cat. No. 7615, *pro analysi*, assay of RbCl ≥ 99.5 mass per cent; rubidium chloride, Ultrapure, Alfa Inorganics, Cat. No. 87632; rubidium chloride, Suprapur, Merck, Cat. No. 7622; rubidium bromide, Ultrapure, Alfa Inorganics, Cat. No. 87631; rubidium iodide, Ultrapure, Alfa Inorganics, Cat. No. 87633.

^a To whom correspondence should be addressed.

The molar masses M and the densities ρ used throughout this study are as follows: $M/(\text{g} \cdot \text{mol}^{-1})$: KCl, 74.5513; RbCl, 120.9208; RbBr, 165.3718; RbI, 212.3723; H_2O , 18.0152; $\rho/(\text{g} \cdot \text{cm}^{-3})$: KCl, 1.988; RbCl, 2.76; RbBr, 3.35; RbI, 3.55.

The water used was doubly distilled from glass vessels. The first distillation was from potassium permanganate. As a rule, distilled water was left standing in a closed glass vessel at least for several days before use.

CALORIMETRIC SYSTEM AND PROCEDURE

The enthalpies of solution were measured with an LKB-8700 Precision Calorimetry System equipped with a 100 cm^3 reaction vessel.⁽⁹⁾ The maximum stirring speed was used in the reaction vessel. The conversion between the resistance of the thermistor and temperature was determined in the range 297 to 299 K by a recently calibrated Hewlett-Packard quartz thermometer.

Solid samples were prepared by gently crushing and then heating in a furnace on a ceramic glazed dish at 773 K for 5 h. Exceptions to this procedure were the RbCl Suprapur Merck samples Nos. 2, 4, and 5 which were heated for 28 h, and the RbI Alfa samples which were heated at 673 K for 6 h. The particle size is unknown because the samples were not screened.

The ampoules were filled immediately upon cooling of the solid sample in the air, except for the KCl sample from Alfa which was filled under a stream of nitrogen. The ampoules themselves were prepared by being dried in an oven at 393 K and allowed to come to equilibrium under room conditions before filling. The ampoules were closed with the supplied rubber stopper, but not sealed with wax as this was found to be unnecessary. Samples were often left sealed in ampoules for several days before use.

Two methods of filling the reaction vessel with a known mass of water were employed. In one, by removing the vessel, the mass difference between the empty and filled vessel was determined. Dr G. Oloffson suggested,⁽¹⁰⁾ on the basis of her experience, that a simpler method is to employ a calibrated 100 cm^3 pipette to transfer a known mass of water to the vessel. This latter method was used on all of the Alfa samples and on the RbCl samples of Merck Suprapur nos. 4 and 5, where the mass of water was (99.61 ± 0.02) g.

An electrical calibration was performed both before and after the breaking of each ampoule. Because all the reactions discussed here are endothermic, this arrangement enabled the two calibrations to be performed over approximately the same temperature range as the experiment itself. The jacket temperature was maintained at about 298 K, with the circulating water at about 296 K. Temperature changes^(11,12) of the calorimeter were expressed in terms of $\ln(R_1/R_2)/(\ln R_1 \ln R_2)$, where R_1 and R_2 are, respectively, the initial and final resistances corrected for heat leakage; R_1 and R_2 for the solution experiment were calculated by extrapolating to the time of 63 per cent of the corrected temperature rise. For calibrations, extrapolations were taken to 50 per cent of the corrected temperature rise. The procedure is described in detail in references 12 and 13. The end of the main period of the experiment and calibration was taken as that time when the slope of the change in R with time became

constant. Resistance-time points were determined with a frequency of about 2 min^{-1} , and continued until about 5 min after the end of each main period.

3. Results

The results obtained for KCl, RbCl, RbBr, and RbI are shown in table 1 where the column headings have the following meanings: w is the mass of the solute; m is the molality of the solution after the solution experiment; ΔH is the enthalpy change; T_{mean} is the average of the initial and final temperatures of the solution experiment; $\Delta H_m(298.15 \text{ K})$ is the molar enthalpy of solution of the solute, corrected for sample impurities, enthalpy of vaporization of water into the air space in the ampoule, and adjusted to 298.15 K. $\Delta H^\infty(298.15 \text{ K})$ is the enthalpy of solution calculated to conditions of infinite dilution. The ΔH values, after being corrected for the vaporization effect, were then multiplied by the impurity factor as follows: KCl, Merck, 1.0007; RbCl, Suprapur Merck, 0.9994; RbCl, Merck, 0.9993. The Alfa samples all had an impurity factor of 1.0000. The impurity factor was defined as the ratio of the enthalpy of solution of a given mass of the pure compound to the enthalpy of solution of the same total mass of substance but including impurities. The impurity corrections for RbCl and KCl were calculated using literature values for the enthalpies of solution,⁽¹⁴⁾ based on the assumption that all of the non-metallic impurities were present in the form of potassium or rubidium compounds, and all of the metallic impurities were present in the form of chlorides. It is assumed that each compound of an impurity went into solution at infinite solution. The correction of the enthalpy for impurities is open to discussion. It does, however, enable a comparison to be made between samples of different purities.

The enthalpy of evaporation of water to fill the air space in the ampoule was taken as $0.0531 \text{ J} \cdot \text{cm}^{-3}$.⁽¹⁵⁾

The adjustment to 298.15 K was performed as follows:⁽¹⁶⁾

$$\Delta H_m(298.15 \text{ K}) - \Delta H_m(T_{\text{mean}}) = \Delta C_{p,m}(298.15 \text{ K} - T_{\text{mean}}),$$

where $\Delta C_{p,m} = (C_{\phi,m} - C_{p,m})$ and $C_{\phi,m}$ is the apparent molar heat capacity of the dissolved salt at the given molality and $C_{p,m}$ is the molar heat capacity of the salt before solution. Literature values of $C_{p,m}$,^(14,17) $C_{\phi,m}$ (Rb salts),⁽¹⁸⁾ and $C_{\phi,m}$ (KCl),⁽¹⁶⁾ were employed. The extrapolation to infinite dilution used literature enthalpies of dilution for KCl,⁽⁶⁾ and the rubidium compounds.⁽¹⁸⁾

4. Discussion

The analysis of the KCl samples was performed as a check against calorimetric bias in our measurement system. In 1974 IUPAC recommended⁽¹⁹⁾ the following change of state as a standard test reaction:



where the " \pm term allows for the effect of various ways of preparing the sample". The values obtained in the present study, adjusted⁽⁶⁾ to this composi-

TABLE 1. Calorimetric results for enthalpies of solution

run	$\frac{w}{g}$	$\frac{m}{\text{mol} \cdot \text{kg}^{-1}}$	$\frac{\Delta H}{J}$	$\frac{T_{\text{mean}}}{K} - 273.15$	$\frac{\Delta H(298.15 \text{ K})}{J \cdot \text{mol}^{-1}}$	$\frac{\Delta H^{\circ}(298.15 \text{ K})}{J \cdot \text{mol}^{-1}}$
KCl (Alfa)						
1	0.52362	0.07051	123.306	25.21	17585	17271
2	0.52516	0.07072	122.976	25.20	17485	17171
3	0.54810	0.07381	128.896	25.20	17560	17242
4	0.55366	0.07456	130.348	25.20	17577	17263
5	0.57193	0.07702	134.273	25.21	17531	17213
6	0.57456	0.07737	135.185	25.18	17564	17246
7	0.61087	0.08226	143.913	25.25	17598	17276
						17240 ± 28^a
KCl (Merck)						
1	0.52621	0.06722	123.005	25.21	17535	17192
2	0.63752	0.08184	149.544	25.14	17456	17146
3	0.69026	0.08803	161.653	25.04	17472	17146
4	0.65723	0.09214	154.360	25.23	17531	17209
5	0.74760	0.09510	175.376	25.26	17539	17205
6	0.78548	0.11120	184.288	25.41	17585	17255
						17192 ± 34^a
RbCl (Alfa)						
1	0.42965	0.03567	61.149	25.18	17230	16987
2	0.53642	0.04453	76.232	25.21	17209	16958
3	0.56301	0.04674	79.785	25.20	17163	16903
4	0.62628	0.05200	89.186	25.21	17251	16983
5	0.71921	0.05971	102.596	25.24	17284	17012
6	0.84078	0.06980	119.959	25.19	17280	17000
7	0.95127	0.07898	135.557	25.22	17263	16979
						16975 ± 27^a
RbCl (Merck Suprapur)						
1	0.66574	0.05211	93.805	25.17	17050	16786
2	0.69971	0.05556	98.818	25.12	17079	16811
3	0.81790	0.06401	116.503	25.08	17221	16945
4	0.82115	0.06817	116.742	25.21	17209	16933
5	0.86670	0.06838	122.436	25.12	17100	16820
6	0.96805	0.08249	137.946	25.10	17234	16945
7	1.23125	0.09667	174.171	25.17	17121	16866
8	1.52695	0.12098	216.966	25.22	17205	16912
						16877 ± 46^a
RbCl (Merck)						
1	0.34776	0.03018	49.179	25.31	17125	16895
2	0.61234	0.05029	87.023	25.00	17167	16899
3	0.67398	0.05970	95.395	25.43	17171	16899
4	0.79491	0.06726	112.579	25.37	17171	16891
5	1.02894	0.07999	145.825	25.29	17171	16887
6	0.95454	0.08051	134.942	25.04	17083	16799
7	0.94974	0.08248	135.281	25.18	17238	16954
8	1.17609	0.10082	167.452	25.24	17242	16954
9	1.19474	0.10432	169.799	25.32	17226	16933
10	1.26090	0.10818	179.494	25.28	17246	16954
11	1.55991	0.12888	221.572	25.34	17221	16924
						16908 ± 27^a

TABLE 1—continued

run	w g	m mol·kg ⁻¹	ΔH J	$T_{\text{mean}} - 273.15$ K	$\Delta H(298.15 \text{ K})$ J·mol ⁻¹	$\Delta H^\circ(298.15 \text{ K})$ J·mol ⁻¹
RbBr (Alfa)						
1	0.62622	0.03802	84.550	25.21	22359	22167
2	0.71572	0.04345	96.738	25.29	22397	22200
3	0.98646	0.05988	133.574	25.27	22435	22230
4	1.06360	0.06457	143.934	25.23	22414	22209
5	1.17872	0.07156	158.992	25.19	22334	22129
6	1.20791	0.07333	163.080	25.25	22368	22167
						22184 ± 30 ^a
RbI (Alfa)						
1	0.87904	0.04155	106.646	25.20	25790	25602
2	1.07132	0.05064	129.608	25.29	25736	25548
3	1.12570	0.05321	136.403	25.48	25807	25623
4	1.21322	0.05735	147.143	25.32	25807	25619
5	1.44184	0.06816	174.636	25.32	25773	25594
						25597 ± 27 ^a

^a Twice the standard deviation of the mean.

tion, yield the results: Alfa: $\Delta H(298.15 \text{ K}) = (17581 \pm 28) \text{ J} \cdot \text{mol}^{-1}$; Merck: $\Delta H(298.15 \text{ K}) = (17531 \pm 34) \text{ J} \cdot \text{mol}^{-1}$. The agreement is within the limits of error of the IUPAC value. Two studies^(1,2) of the NBS sample of RbCl reveal agreement between the Alfa sample studied here and the NBS sample, within our limits of error. No investigations of comparable accuracy were found for RbBr or RbI.

One of the authors (R. Weintraub) is grateful to Dr Gerd Olofsson for a helpful discussion on calorimetry during her short stay in Jerusalem. The authors are indebted to Mr Moshe Golden for preparing the computer program.

REFERENCES

- Montgomery, R. L.; Melaugh, R. A.; Lau, C.-C.; Meier, G. H.; Grow, R. T.; Rossini, F. D. *J. Chem. Eng. Data* **1978**, 23, 245.
- Johnson, G. K.; Gayer, K. H. *J. Chem. Thermodynamics* **1979**, 11, 41.
- Abrosimov, V. K.; Ionov, A. V.; Krestov, G. A. *Radiokhimiya* **1977**, 19, 862.
- Paoletti, P.; Vacca, A. *Trans. Faraday Soc.* **1964**, 60, 50.
- Wu, Y.-C.; Friedman, H. L. *J. Phys. Chem.* **1966**, 70, 501.
- Parker, V. B. *Thermal Properties of Aqueous Uni-Univalent Electrolytes*. Natl. Bur. Stand. (U.S.): Washington, D.C. **1965**.
- Amigó, J. M.; Carreras, G.; Cesari, E.; Navarro, J.; Reventós, M. M.; Rubio, A.; Torra, V. *Conference International Thermodynamics Chimie 4th* **1975**, 1, 209.
- Novoselev, N. P.; Ryabchenko, O. I.; Mishchenko, K. P.; Klyueva, M. L. *Zh. Prikl. Khim.* **1975**, 48, 2296.
- Sunner, S.; Wadsö, I. *Sci. Tools* **1966**, 13, 1.
- Olofsson, G. Personal communication.
- Gunn, S. R. *J. Chem. Thermodynamics* **1971**, 3, 19.
- Wadsö, I. *Sci. Tools* **1966**, 13, 33.

13. White, M. P. *The Modern Calorimeter*. The Chemical Catalog Company: New York. **1928**.
14. Rossini, F. D.; Wagman, D. D.; Evans, W. H.; Levine, S.; Jaffe, I. *Natl Bur. Stand. (U.S.) Circ. No.* 500. **1950**.
15. Gunn, S. R. *J. Chem. Thermodynamics* **1970**, 2, 535.
16. Montgomery, R. L.; Melaugh, R. A.; Lau, C.-C.; Meier, G. H.; Chan, H. H.; Rossini, F. D. *J. Chem. Thermodynamics* **1977**, 9, 915.
17. *JANAF Thermodynamical Tables*. Dow Chemical Co.: Midland, Michigan. **1975**.
18. Fortier, J.-L.; Leduc, P.-A.; Desnoyers, J. E. *J. Solution Chem.* **1974**, 3, 323.
19. Herington, E. F. G.; Cox, J. D. *Pure Appl. Chem.* **1974**, 40, 399.