Thermochimica Acta, 46 (1981) 47—51
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

INTEGRAL HEAT OF DISSOLUTION OF POTASSIUM CHLORATE IN WATER AT 298.15 K

V. PEKÁREK and V. VACEK

Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences, 160 00 Prague 6 (Czechoslovakia)

S. KOLAŘÍK

Chemopetrol, Research Institute of Inorganic Chemistry, 400 00 Ústí nad Labem (Czechoslovakia)

(Received 20 November 1980)

ABSTRACT

The heat of dissolution of potassium chlorate in water at 298.15 K has been measured on an LKB 8700-1 calorimeter in the concentration range 0.063—0.659 m. The concentration dependence of the measured data was fitted by an empirical equation

$$\Delta H_m \text{ (kJ mole}^{-1}) = 41.353_8 + 1.862_6\, m^{1/2} - 6.430_0\, m$$

which was derived from our and Andauer—Lange data. The heat of crystallization calculated from this dependence was $\Delta H_{\text{cryst.}} = 34.7 \pm 0.5$ kJ mole^{-1}, which agrees with data calculated for potassium chlorate from solubility and activity data.

INTRODUCTION

Old measurements of dissolution and/or dilution heats of potassium chlorate at temperatures between 283 and 291 K are summarized in refs. 1 and 2. Dilution heats of potassium chlorate in water at 298.15 K in the diluted solutions were precisely measured by Andauer and Lange [3] (27 values). Integral endothermic dissolution heats in diluted solutions (0.0045—0.017 m) were measured by Nelson et al. [4] (six values) with uncertainty, estimated by us as about 147 J. Nelson et al's [4] recommended value for the integral heat of dissolution of potassium chlorate in water at infinite dilution (ΔH^0) is 41.38 ± 0.25 kJ mole^{-1} and is used in recent standard tables [5,6]. The value of ΔH^0 is in fairly good agreement with the value previously published by Gopal [7] (41.67 kJ mole^{-1}); however, no details of the experimental method used are available. Integral dissolution heats of potassium chlorate in water in the concentration range 0.0066—0.061 m were measured by Medvedev et al. [8] (nine values); it seems that these data suffer from uncertainty by about 272 J.

From the published data we can assume that for the ΔH^0 calculations the most reliable concentration dependence in the region of very dilute solutions ($m < 0.1$) given by Andauer and Lange [3] would be advantageous. However, the molality dependence of the dissolution enthalpy of potassium chlorate in water in the more concentrated solutions has not yet been measured systematically. Only four values of the integral dissolution heats in the range 0.20—0.56 m solutions can be obtained from the data of Andauer and Lange [3] by combining their integral dilution heats with a value of $\Delta H^0 =$ 41.38 kJ mole^{-1} mentioned above.

The present work deals with the measurement of the enthalpy of dissolution of potassium chlorate in water at 298.15 K as a function of the molality in the concentration range 0.063—0.659 m, with the aim of calculating the most reliable value of the heat of crystallization of the compound studied.

EXPERIMENTAL

Reagent grade potassium chlorate (Lachema Brno, Czechoslovakia) was triply recrystallized from redistilled water, dried in an electric oven at 310 K, and then in a desiccator with phosphorus pentoxide. Water redistilled from silica was used in all experiments.

The LKB calorimeter, type 8700-1 with 25 cm^3 and 100 cm^3 glass cells, was used for the measurements. The integral heats were measured by dissolving an appropriate amount of the salt either in pure water or in the solution of potassium chlorate in water of given concentration. A solution of initial molality m_1 (m_1 ranged from 0.11 to 0.64 m) was used as a solvent in more concentrated systems instead of pure water. The duration of these experiments did not exceed 30 min and the results were evaluated by the standard Regnault—Pfaundler method [9]. For each measurement two electric calibrations were performed and the corresponding heats of dissolution calculated; the resulting difference between the two evaluated heats was taken as an uncertainty of the heat measurement. The molality 0.700 mole kg^{-1} was taken as the saturation concentration [10] at 298.15 K.

RESULTS AND DISCUSSION

The integral dissolution heat of potassium chlorate for the final concentration, m_2, was calculated from the enthalpy effect measured, Q, which is connected with dissolving Δn_2 moles of potassium chlorate in the solution of concentration m_1 containing n_1 moles of the salt, and giving a final solution concentration m_2 from the equation

$$\Delta H_{m_2} = (Q + n_1 \Delta H_{m_1})/(n_2 + \Delta n_2) \qquad (1)$$

The measured and calculated values of ΔH_{m_2} are given in Table 1. The concentration dependence $\Delta H_m(m)$

$$\Delta H_m \text{ (kJ mole}^{-1}) = 41.371_4 + 2.042_2\, m^{1/2} - 6.654_7\, m \qquad (2)$$

which follows from fitting the data set given by Andauer and Lange [3] was used to evaluate ΔH_{m_1} in eqn. (1). Resulting values of ΔH_{m_2}, presented in Table 1, are closely spread (with maximum difference between measured and

TABLE 1

Measured and calculated [see eqn. (4)] integral dissolution heats for potassium chlorate in water at 298.15 K

Molality (mole of the salt/ 1 kg water)		$\Delta H_{m_{\text{exp.}}}$ (kJ mole^{-1})	$\Delta H_{m_{\text{calc.}}}$ (kJ mole^{-1})	ϵ (%)	$L_{m_{\text{calc.}}}$ (kJ mole^{-1})
m_1	m_2				
0	0.0630	41.024	41.416	−0.95	41.245
0	0.0746	41.296	41.383	−0.21	41.158
0	0.0778	41.204	41.373	−0.41	41.133
0	0.1100	41.530	41.264	0.64	40.866
0	0.1160	41.254	41.242	0.03	40.814
0.1064	0.1580	40.920	41.078	−0.39	40.432
0.1064	0.1998	40.857	40.902	−0.11	40.033
0.1064	0.2130	40.857	40.844	0.03	39.904
0.1064	0.2550	40.585	40.655	−0.17	39.485
0.2539	0.2980	40.501	40.454	0.12	39.047
0	0.3610	40.229	40.152	0.19	38.390
0.2539	0.3610	40.020	40.152	−0.33	38.390
0.2539	0.3990	39.957	39.965	−0.02	37.987
0.3836	0.4470	39.790	39.725	0.16	37.473
0.3913	0.4490	39.790	39.715	0.19	37.452
0.3273	0.4630	40.459	39.644	2.06	37.301
0.3876	0.4475	39.681	39.722	−0.10	37.468
0.4947	0.5364	38.953	39.269	−0.80	36.502
0.3906	0.5426	39.091	39.237	−0.37	36.434
0.3896	0.5528	39.367	39.184	0.47	36.322
0.3906	0.5798	39.179	39.044	0.35	36.025
0.5528	0.6084	39.413	38.895	1.33	35.709
0.6084	0.6246	38.698	38.810	−0.29	35.529
0.5745	0.6237	38.564	38.814	−0.65	35.539
0.3896	0.6425	38.505	38.715	−0.54	35.331
0.5745	0.6492	38.673	38.680	−0.02	35.256
0.6425	0.6587	38.388	38.630	−0.63	35.150

calculated values below 1% excluding two points) to the correlation

$$\Delta H_m \text{ (kJ mole}^{-1}\text{)} = 40.568_5 + 4.840_9\, m^{1/2} - 9.001_0\, m \qquad (3)$$

These results represented by eqn. (3) are in very good agreement with previously published data given by Andauer and Lange [3] and by Nelson et al. [4]. The maximum relative difference between calculated enthalpies from eqns. (2) and (3) is less than 0.1%. In fact, a similar correlation

$$\Delta H_m \text{ (kJ mole}^{-1}\text{)} = 41.353_8 + 1.862_6\, m^{1/2} - 6.430_0\, m \qquad (4)$$

deduced from all data measured (our results and data presented in refs. 3 and 4) yields to a very close course, which differs from eqn. (3) several times less than is the experimental uncertainty of our measured data. Even our experimental results in more concentrated systems are less accurate compared with the data of Andauer and Lange [3] for more dilute systems; we find the conformity and mutual consistency of both concentration correlations satisfying. Differences between correlation eqns. (2), (3), and (4) are negligible so that for the calculation of $(\Delta H_{m_2})_{\text{calc.}}$ and ϵ in Table 1 the correlation eqn. (4) has been used.

The value of the differential heat of dissolution at saturation

$$L_{m_s} = \Delta H_{m_s} + m_s \left.\frac{\partial \Delta H_m}{\partial m}\right|_{m=m_s} \tag{5}$$

is of special interest, being numerically equal to the heat of crystallization of the potassium chlorate. No experimental value for the heat of crystallization of this compound was found in the literature. However, from the solubility data, Nakayama [11] has estimated an exothermic value of 35.19 kJ mole^{-1} for the heat of crystallization of potassium chlorate; the saturation solubility, $m_s = 0.700$, and the concentration—temperature dependence

$$(\partial \ln m_s/\partial T^{-1}) = -3020 \tag{6}$$

were taken from tables [6,12] and the activity—concentration dependence

$$[1 + (\partial \ln \gamma_\pm/\partial \ln m)_{m_s}] = 0.70 \tag{7}$$

from the work of Jones [13]. Using the equation

$$\Delta H_{\text{cryst.}} = \nu R[1 + (\partial \ln \gamma_\pm/\partial \ln m)_{m_s}].\,(\partial \ln m/\partial T^{-1}) \tag{8}$$

the above value was calculated supposing the total dissociation of the electrolyte at its saturation concentration. In the same way it is possible to determine a value of 34.69 ± 0.21 kJ mole^{-1} for the heat of crystallization of potassium chlorate in water at 298.15 K, using the solubility data from

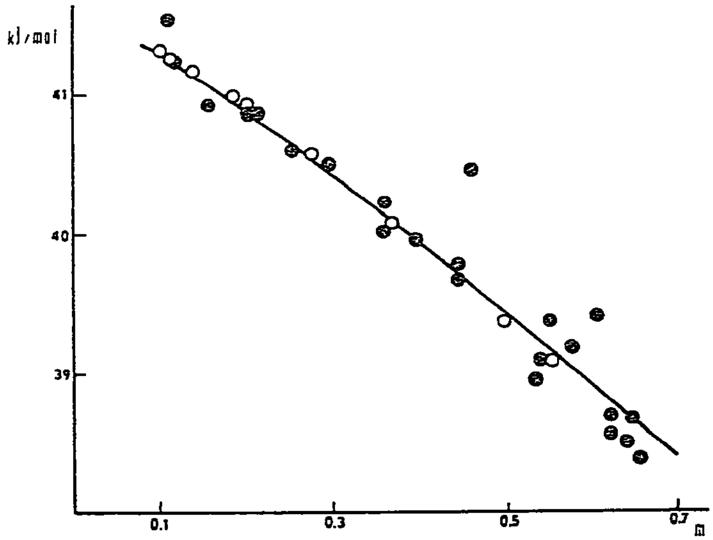

Fig. 1. Dissolution enthalpy for potassium chlorate in water at 298.15 K as a function of molality. ●, Present work; ○, data of Andauer and Lange [3].

Broul et al.'s tables [10], and the concentration dependence of osmotic coefficients from the data of Robinson and Stokes [14].

From the concentration dependence of the differential heat of dissolution (see Fig. 1) calculated from integral dissolution heat data measured by us, the value for the differential heat of dissolution at saturation concentration was determined

$$L_{m_s} = -\Delta H_{\text{cryst.}} = 34.7 \pm 0.5 \text{ kJ mole}^{-1}$$

This heat of crystallization determined from the heats of dissolution is in surprisingly good agreement with previously estimated values from solubility and activity data. Assuming this mutual consistency, as well as the fact that our dissolution heat measurements are in satisfactory accordance with those given by Andauer and Lange [3], we consider this determined value of the heat of crystallization of potassium chlorate to be correct.

REFERENCES

1 Gmelin's Handbuch der Anorganischen Chemie, Verlag Chemie, Berlin, 1938, Kalium, p. 492.
2 E.V. Bricke and A.F. Kapustinskii (Eds.), Termicheskie Konstanty Neorganischeskich Veshchestv, Izdatelstvo Akademii Nauk S.S.S.R., Moscow, Leningrad, 1947, p. 323.
3 M. Andauer and E. Lange, Z. Phys. Chem., Abt. A, 165 (1933) 89.
4 T. Nelson, C. Moss and L.G. Hepler, J. Phys. Chem., 64 (1960) 376.
5 V.B. Parker, Thermal Properties of Aqueous Uni-univalent Electrolytes, NSRDS-NBS 2, U.S. Government Printing Office, Washington D.C., 1965.
6 G. Beggerow, Heats of Mixing and Solution, in Kl. Schäfer (Ed.), Landolt-Börnstein New Series, Group IV, Vol. 2, Springer-Verlag, Berlin, 1976.
7 R. Gopal, Z. Anorg. Allg. Chem., 278 (1955) 46.
8 V.A. Medvedev, M.E. Efimov, O.A. Davina and G.N. Klevaychuk, VINITI Rep. No 3318, Moscow, 1974, UDK 536.65.
9 I. Wadsö, Sci. Tools, 13 (1966) 33.
10 M. Broul, J. Nývlt and O. Söhnel, Solubility in Inorganic Two-Component Systems, Elsevier, Amsterdam, 1980.
11 H. Nakayama, Bull. Fac. Eng., Yokohama Natl. Univ., 19 (1970) 29.
12 A. Seidell and F.W. Linke, Solubilities of Inorganic and Metalo-organic Compounds, Van Nostrand, New York, 1953, Am. Chem. Soc., Washington, 1965.
13 J.H. Jones, J. Am. Chem. Soc., 66 (1944) 1672.
14 R.A. Robinson and R.H. Stokes, Electrolyte Solutions, Butterworths, London, 1959.