

DIFFERENTIAL HEATS OF DISSOLUTION OF POTASSIUM NITRATE IN WATER AT 298.15 K NEAR THE SATURATION CONCENTRATION

Stanislav KOLAŘÍK^a, Vladimír PEKÁREK^b and Jiří HOSTOMSKÝ^b^a *Chemopetrol, Research Institute of Inorganic Chemistry,
400 60 Ústí nad Labem and*^b *Institute of Inorganic Chemistry,
Czechoslovak Academy of Sciences, 160 00 Prague 6*

Received June 2nd, 1981

Differential heats of dissolution of potassium nitrate in water at 298.15 K were measured on an 8 700 LKB calorimeter over a molality range 3–3.5 mol/kg. The dependence of the differential heat of dissolution, ΔL_m (kJ/mol), on the molality can be described over the above range by the relation $\Delta L_m = -33.93_3 + 3.63_3 m$. The value of the endothermic last dissolution heat obtained by extrapolation to the saturation concentration of 3.75 mol/kg was found to be -20.30_3 kJ/mol, with a standard deviation of 0.37 kJ/mol.

Although potassium nitrate is among the most commonly used salts, data on its integral heats of solution and dissolution as determined by various workers differ considerably, particularly in the region of concentrated solutions near saturation. Measurements on dilute solutions were performed by Kangro and Groenvald¹, Mondain-Monval², Naudé³, and Nernst and Orthmann⁴. The report of Parker⁶ lists older, very precise data measured by Lange and Monheim⁵. Tanjewska-Osinska and Logwinienko⁷ have published integral data for temperature and molality ranges of 278.15–298.15 K and 0–3.41 mol/kg, respectively. Integral heats of dissolution for nearly saturated and supersaturated solutions have been reported by Shmagin and Shidlovskii⁸ and Khrenova and Akhumov⁹. The published data on integral heats are mutually inconsistent, with the inconsistency increasing markedly as the solutions approach saturation¹⁰.

The concentration dependence of differential dissolution heats of potassium nitrate has been published in graphical form by Rychlý¹⁰; unfortunately, the paper does not give tabular data on the measured pseudodifferential heats. This concentration dependence is in disagreement with those obtained by recalculating integral data measured by previous authors^{6–9}. Extrapolations to the saturation concentration, *i.e.* values of last dissolution heat, are within an uncertainty of $\pm 10\%$.

In this work we measured the concentration dependence of the differential heat of dissolution of potassium nitrate in the region of concentrated solutions, with the aim of obtaining reliable data for the determination of last dissolution heat.

EXPERIMENTAL

Potassium nitrate of analytical grade (Lachema Brno, Czechoslovakia) was recrystallized five times from redistilled water, dried in an electric oven at 310 K, and then stored in a desiccator over phosphorus pentoxide for several weeks. Glass LKB ampoules with roughly weighed

amounts of the salt were left standing in an atmosphere of saturated solution of magnesium nitrate at 298 K (c. 50% relative humidity) until constant weight (~ 10 min), then weighed and closed with silicon rubbers.

The measurements were carried out on an 8 700-l LKB calorimeter with glass reaction cells of 100 cm³ capacity, over a molality range of 3.1–3.5 mol/kg. The weight ratio of solution to dissolved salt was 115–117 g: 380–480 mg. The time required for the salt to dissolve in the most concentrated systems did not exceed 20 min. Electrical heating of the calorimeter was calibrated by the reaction heat of tris(hydroxy-methyl)-amino-methane (NBS-724a standard reference material) with 0.1 mol/kg HCl (ref.¹¹). All solutions used were made up from water redistilled in a quartz apparatus¹².

The recorded resistance-time (R - t) curve was evaluated numerically on a computer, using the standard Regnault-Pfaundler method¹³. The R - t plot was divided into sections representing the initial and final periods of experiment. Fitting second-degree polynomials to these sections and extrapolating in terms of the Regnault-Pfaundler method yielded corrected values of ΔR , heat transfer coefficients, and mean values \bar{R} for each calibration and experiment. The heat effect, Q (kJ), corresponding to heat changes during dissolution, was calculated from the equation $Q(\bar{R}/\Delta R)_{\text{exp}} = Q_{\text{calibr}}(\bar{R}/\Delta R)_{\text{calibr}}$, where $Q_{\text{calibr}} = t_k R_k I^2$, with t_k denoting the heating time in calibration, R_k the resistance of the calibration heater, and I the current flowing through the heater.

As discussed below, improper identification of the final period may introduce errors in the results, especially in experiments with slow dissolution (dissolution in nearly saturated solutions).

RESULTS AND DISCUSSION

The resulting values of the pseudodifferential heats of dissolution, ΔL_m (kJ/mol), of potassium nitrate in water at 298.15 K are listed in Table I as a function of the mean molality, \bar{m} (arithmetic average of the initial concentration and the final con-

TABLE I

Differential heats of dissolution, ΔL , of potassium nitrate in water at 298.15 K. \bar{m} mean molality; Δ deviations from the linear fit (Eq. 1); δ error due to electrical calibration

m_1 mol/kg	m_2 mol/kg	\bar{m} mol/kg	Δm %	$-\Delta L_m$ kJ/mol	$\pm \delta$	Δ kJ/mol
3.2438	3.2972	3.2705	1.65	22.15	0.01	+0.10
3.2438	3.2982	3.2710	1.68	22.01	0.14	-0.04
3.2438	3.2964	3.2701	1.62	22.20	0.04	+0.15
3.4468	3.4945	3.4707	1.38	20.73	0.02	-0.56
3.4468	3.4945	3.4707	1.38	21.73	0.02	+0.41
3.4468	3.4904	3.4686	1.26	21.40	0.01	+0.08
3.0599	3.1069	3.0834	1.54	22.43	0.16	-0.29
3.0599	3.1057	3.0828	1.50	22.91	0.09	+0.18

centration on dissolution of the salt). The measurements were carried out for three concentration levels in the region of highly concentrated solutions. Effort was made to use as concentrated solutions as possible, and thus to reduce the uncertainty in extrapolation of the $\Delta L_{\bar{m}}$ vs \bar{m} curve to the saturation concentration to a minimum. Several measurements were performed for each concentration to allow a check on error and methodology of pseudodifferential heat measurement under the given conditions. The differential heat for the mean concentration \bar{m} was calculated from the relation $\Delta L_{\bar{m}} = QM/g$, where M is the molecular mass of KNO_3 and g is the weighed amount of salt. An assumption underlying this relation is that the concentration changes during dissolution are negligibly small, approaching the conditions where the salt is dissolved in a solution of infinitely large volume, causing no change in the concentration. Justification of this assumption was tested by handling the measured data also as strictly integral data and calculating differential heats from the resulting values. From Table I the concentration change due to dissolution of the salt in the given system is seen to lie within the range 1.2–1.7%. Since the difference in the heat values obtained by the two different calculations is much below the error of the heat measurement, we can consider these as differential heats.

The results given in Table I can be fitted, within the given range of molalities, to the equation

$$\Delta L_{\bar{m}} = -33.93_3 + 3.63_5 \bar{m}. \quad (1)$$

The deviations, Δ , for fitting the data to this equation are included in Table I.

Fig. 1 provides a comparison between our and other authors' results. The integral heat data measured by Parker⁶ (curve 1) and Taniewska-Osinska⁷ (curve 2) are in good agreement in dilute region ($m < 2$ mol/kg), with increasing concentration, however, uncertainty of measurements markedly increases. The inconsistency of the data becomes even more pronounced on recalculation to differential heats (curves 3 and 5), the uncertainty of last dissolution heat determination being now at least 5 kJ/mol. The differential heats measured by us (curve 4) lie between the data of the above authors^{6,7}, and are in very good agreement with the data of Rychlý¹⁰.

A summary of data on potassium nitrate dissolution heats presented by Rychlý¹⁰, and Fig. 1 of this paper show that the heats as measured in various laboratories differ in magnitude by multiples of experimental errors in the individual data sets. The large differences seem to arise from differing methods of the salt preparation, performances of experiments and experimental data evaluations rather than from experimental errors inherent in the instruments used. Pautov and Jermolae¹⁴ arrived at the same conclusion by analyzing the precision of published data on integral dissolution heats for dilute solutions of equally simple $\text{KCl-H}_2\text{O}$ system. It was thus of interest to examine the extent to which properties of the salt, its weight, solution concentration, performance and evaluation of experiments affect the uncertainty in the measured data.

The handling of the salt before weighing has been described in detail in the previous section. The weighing was considered satisfactory if variations in the weight during 5 to 10 min did not exceed ± 0.015 mg. Total change in the weight of ampoule containing a sample in the time between withdrawal of the sample from the desiccator and termination of weighing was not greater than 0.1 mg. Thus, the error incurred in the weighing of *c.* 400 mg of the salt did not exceed 0.03%, a value much below the expected experimental error of the calorimetric method. The maximum difference in the weights of solutions pipetted into calorimetric cells in parallel experiments was 0.05 g, introducing a maximum error of 0.05% when pipetting *c.* 115 g of the solution. Since ΔL_m shows no pronounced concentration dependence, this error source may be neglected.

A potential source of systematic error may be the difference in the course of calibration and of the experiment proper, especially in dissolution into concentrated solutions where the heat evolution is very slow and difficult to simulate. Therefore,

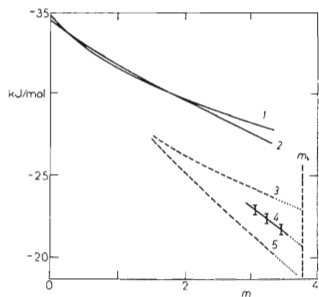


FIG. 1

Concentration dependences of integral and differential heats of dissolution (kJ/mol) of potassium nitrate in water at 298.15 K. *m* molality (mol/kg); m_s molality of saturated solution at 298.15 K; 1 integral dissolution heat data of Parker⁶; 2 integral dissolution heat data of Taniewska-Osinska and Logwinienko⁷; 3 differential heats calculated from integral data of Parker⁶; 4 our pseudo-differential data; 5 differential heats calculated from integral data of Taniewska-Osinska and Logwinienko⁷

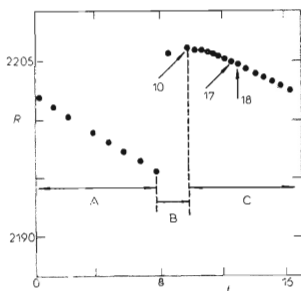


FIG. 2

Record of measurement of pseudodifferential heats of potassium nitrate dissolution in a solution of 3.4692 mol/kg molality at 298.15 K on LKB calorimeter. *R* resistance (Ω); *t* time (min); A initial period, B main period, C final period

we performed calibrations at various intensities of heating. The differences δ in the values of ΔL_m due to differences in the $(\Delta R/\bar{R})_{\text{calibr}}$ at various heating intensities did not exceed 0.2 kJ/mol (Table I), the average δ value over all experimental points being 0.06 kJ/mol. In carefully conducted experiments the error introduced by calibration should not exceed significantly the above average value of ± 0.06 kJ/mol, i.e. 0.3% of ΔL_m , and thus should not markedly affect the measured dissolution heats.

Significant errors may, however, arise as a result of improper identification of the start of the final period, or of insufficient number of experimental points in this period. The significance of a correct estimate of the start of the final period for dissolution heat calculation by the Regnault-Pfaundler method¹³ is illustrated in Fig. 2 which shows a record of measurement of potassium nitrate dissolution heat in a solution of 3.4692 mol/kg molality. The initial period (A) characterizes the operation of the calorimeter after completing the first calibration experiment; the main period (B) involves the variation in temperature during dissolution after breaking the ampoule containing the salt; the final period (C), whose start has been placed to data point 10, covers temperature changes after the experiment when the dissolution is assumed to be complete. As can be seen from Fig. 2, the choice of the beginning of the final period is uncertain and ambiguous, and will be reflected in the calculated heat values. The shape of the $R-t$ curve also suggests that the number of experimental points in the final period is probably insufficient so that inclusion of a part of the main period in the final period cannot be ruled out. If we choose point 10 as the beginning of the final period, the calculated dissolution heat amounts to -16.54 kJ/mol. Taking point 17 as the beginning, however, we obtain a dissolution heat of -17.13 kJ/mol, a value by c. 3.6% lower. Placing the beginning of the final period to the close, neighbouring point 18 leads to a dissolution heat value by about 0.2% lower (-17.16 kJ/mol). Experimental errors of very good measurements of dilute solutions usually do not exceed this value. All of these dissolution heats are markedly lower, in their absolute values, than the dissolution heat calculated from Eq. (1) for the concentration of 3.4692 mol/kg of solution (-21.34 kJ/mol), a fact which provides evidence that the number of points in the final period is insufficient, leading to inclusion of a part of the main period in the final period.

In view of these considerations we made a series of calculations, shifting the beginning of the final period to longer times until the maximum difference in the resulting heats of dissolution of potassium nitrate in water or a solution of a given concentration for neighbouring experimental points was about 0.03%. Experimental data which failed to fulfil this condition were rejected. This procedure is unnecessary in the region of dilute solutions where the dissolution rate is sufficiently large so that the main and final periods can be safely distinguished. For solutions approaching saturation the analysis of the $R-t$ curve is, however, indispensable since it allows not only to identify exactly the beginning of the final period, to which the resulting dissolution heats are strongly sensitive, but also to specify the limits of experimental

conditions for a given system, which are given by the construction of the calorimeter employed.

The measurement of pseudodifferential heats in the vicinity of saturation permits a relatively accurate extrapolation of the concentration dependence of dissolution heats to the saturation concentration (*i.e.* to a molality of 3.75 mol/kg H₂O regarded¹⁰ as the molality of potassium nitrate saturation at 298.15 K). The value of the last dissolution heat calculated from Eq. (1) is -20.30 kJ/mol. The standard deviation of this extrapolated value is 0.37 kJ/mol.

Alternatively, we determined the value of the last dissolution heat at the concentration of 3.75 mol/kg by combining the eight experimental data points from Table I with a relatively reliable value of first dissolution heat of -35.0 kJ/mol for $m = 0$ taken from refs^{6,7}, and fitting a second-degree polynomial to the resulting data set:

$$\Delta L_m = -35.00 + 4.27m - 9.48 \cdot 10^{-2} m^2. \quad (2)$$

For $m = 3.75$ mol/kg Eq. (2) yields $\Delta L_m = -20.32$ kJ/mol, with a standard deviation of 0.42 kJ/mol, a result identical, on rounding to tenths of kJ/mol, with that obtained from Eq. (1).

REFERENCES

1. Kangro W., Groenvald A.: *Z. Phys. Chem. (Frankfurt am Main)* **32**, 110 (1962).
2. Mondain-Monval P.: *C. R. Acad. Sci.* **176**, 889 (1923).
3. Naudé S. M.: *Z. Phys. Chem. (Leipzig)* **135**, 209 (1928).
4. Nernst W., Orthmann W.: *Sitz. Ber. Akad. Wiss. Berlin*, 1926, 55.
5. Lange E., Monheim J.: *Z. Phys. Chem. A* **150**, 349 (1930).
6. Parker V. B.: *Thermal Properties of Aqueous Uni-univalent Electrolytes*. NSRDS-N.B.S.-2, U.S. Government Printing Office, Washington D.C., 1965.
7. Taniewska-Osinska S., Logwinienko R.: *Soc. Sci. Lodz. Acta Chim.* **18**, 17 (1973).
8. Shmagin L. F., Shidlovskii A. A.: *Zh. Fiz. Khim.* **45**, 1304 (1971).
9. Khrenova T. L., Akhumov E. I.: *Zh. Prikl. Khim.* **42**, 2597 (1969).
10. Rychlý R.: *Chem. Prům.* **27/52**, 291 (1977).
11. Rychlý R., Pekárek V.: *J. Chem. Thermodyn.* **9**, 391 (1977).
12. Stopka P., Vepřek-Šiška J.: *Chem. Listy* **67**, 424 (1973).
13. Wadsö I.: *Science Tools* **13**, 33 (1966).
14. Pautov G. A., Yermolaev M. I.: *Zh. Fiz. Khim.* **53**, 1817 (1979).

Translated by M. Škubalová.