Thermochimica Acta, 104 (1986) 139–145
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ENTHALPIES OF CRYSTALLIZATION OF HALOGENIDES. PART 2. INVESTIGATIONS OF BINARY SYSTEMS

HANS-HEINZ EMONS, GERT WOLF and CHRISTA KROPP
Sektion Chemie, Bergakademie Freiberg, 9200 Freiberg (G.D.R.)

(Received 26 December 1985)

ABSTRACT

In this paper, the indirect experimental determination of crystallization enthalpies by measurement of the dependence on molality of the partial molar enthalpy of solution is discussed. The results obtained for KCl, KBr, KI, NH_4Cl, NH_4Br and RbCl at 298.15 K are compared with values from the literature.

INTRODUCTION

We have already presented a method of measuring the enthalpy of crystallization $\Delta_c H_b$ of a salt b [1], which is based on the direct measurement of the whole enthalpy of solution, and discussed the results obtained for NaCl, $KF \cdot 2H_2O$, KCl, KBr and KI.

For evaluation of the measurements of the whole solution enthalpy it is necessary to known the solubility and the temperature coefficient of solubility of the salt at the temperature of investigation [1]. The necessity of exact knowledge of the solubility data limits the scope of application of this method. With a view to the investigation of crystallization enthalpies of salts in ternary solutions, another method of experimental determination was tested.

Extensive investigations into the determination of enthalpies of crystallization have been published [2–7]. In ref. 6 the errors occurring with different methods are analyzed with the result that errors for the enthalpy of crystallization $\Delta_c H_b = 3\%$ can be obtained only be very exact pseudodifferential measurements of the partial molar enthalpy of solution $\Delta_s H_b$ near the saturation molality m_{sa}.

The theoretical basis of the pseudodifferential method for determining the enthalpy of crystallization results from the fact that $\Delta_c H_b$ corresponds to the negative partial molar enthalpy of solution $\Delta_s H_b$ of the salt b for the borderline case of the saturated solution (the last molar enthalpy of solution $\Delta_s H_{b,sa}$ of the salt b)

$$\lim_{m_b \to m_{b,sa}} \Delta_s H_b(m_b) = \Delta_s H_{b,sa} = -\Delta_c H_b \qquad (1)$$

0040-6031/86/$03.50 © 1986 Elsevier Science Publishers B.V.

By dissolution of very small quantities of b in approximately 10^3 times the quantity of solution (change in molality by addition of less than 3%) it is possible to determine $\Delta_s H_b$ directly: by measurement at different molalities m_b of the solution $\Delta_s H_b = f(m_b)$ can also be defined [2,6,8–11]. In conformity with eqn. (1), $\Delta_c H_b$ is obtained by extrapolating the measurement results to $m_b = m_{b,sa}$.

In this paper, the method we use for the pseudodifferential measurement of $\Delta_s H_b$ is discussed and tested by comparison with well-known molar enthalpies of crystallization.

EXPERIMENTAL

All the calorimetric measurements were carried out in a modified LKB calorimeter (type 8700) at $T = 298.15$ K [1].

The employment of the pseudodifferential method of measurement entails a number of experimental problems. The thermal effect in the dissolution experiment is very small (usually less than 0.1 K), as a minimum addition of salt is essential to a nearly differential measurement. Near the saturation molality m_{sa} the speed of dissolution decreases considerably (the time of dissolution under optimum conditions of agitation for m_b near $m_{b,sa}$ exceeding 60 min). These factors cause the thermal power to be very low over an extended period of time and make the complete acquisition of the thermal effect difficult.

The partial molar enthalpy of solution $\Delta_s H_b$ was measured using the ampoule-technique described previously [1]. 80 ml of solution is placed in the measuring cell of the calorimeter and about 200 mg of the salt to be dissolved is measured into the glass ampoule.

The temperature–time behaviour of the calorimeter cell is recorded by a potentiometric recorder and additionally filed in digital form by a data acquisition system. The change in resistance caused by the variation in temperature of the measuring system is amplified in the form of a diagonal voltage of a Wheatstone bridge by a dc amplifier (input sensitivity $\pm 3 \times 10^{-8}$ V). The output signal of the amplifier is recorded directly by the printer and indicated by a digital voltmeter for digital data acquisition. Under control by a time-event control system (ZES-83) the data are filed in the form of the BCD output information of the digital voltmeter, as independently programmable with respect to number and time interval, for the preliminary, main and after-periods. The ZES-83, in addition, starts the calorimetric experiment or calibration heating during the transition from the preliminary period to the main period.

Owing to the relatively low thermal efficiency at the end of the main period, the transition to the after-period can be determined only by having the measurement data evaluated by a computer, and a special evaluation programme for the filed measurement data was developed.

For the calculation of the temperature difference ΔT, the parameters for the heat flow correction ΔT_{corr} must be ascertained. The change in temperature $\mathrm{d}T/\mathrm{d}t$ of the measuring cell caused by heat exchange is proportional to the difference between the ambient temperature T_{a} and the temperature $T(t)$ in the measuring cell:

$$(\mathrm{d}T/\mathrm{d}t) = K\left[T_{\mathrm{a}} - T(t)\right] \tag{2}$$

Exact knowledge of the exchange constants K and the ambient temperature T_{a} is essential for the calculation of $\Delta T_{\mathrm{corr}}(t)$ on the basis of eqn. (2) and thus for the determination of $\Delta T(t)$ with Regnault-Pfaundler's method [12].

In agreement with simulation calculations for the calorimetric system used and on the assumption of dissolution times higher than 60 min it was found that K must be known with an accuracy of $\pm 3\%$ and T_{a} with ± 0.01 K, if ΔT values of an order of magnitude of 10^{-1} K are to be determined with an accuracy of $\pm 5\%$. An exact determination of K from the temperature–time curve after the experiment will not be possible if the beginning of the effect-free after-period cannot be clearly defined and the difference of $\Delta T_{\mathrm{exp}}(t) = T_{\mathrm{a}} - T(t)$ has already become very small owing to the long dissolution period. Therefore, an independent determination of K for the system to be investigated must be carried out with every investigation. For this purpose, a thermal equilibrium is established at constant heating power, with the difference in temperature between the measuring cell and the environment approximately corresponding to the difference in temperature expected in the dissolution experiment. From the appropriate heating-up and cooling-down curves and the difference in temperature arising, independent values of K, which agree fairly well, are obtained.

The after-period of the calibration experiments, the beginning of which is clearly discernable and in which the difference in temperature ΔT_{exp} is great enough for unambiguously determining the parameters of the exponential cooling function, is used to determine, with sufficient accuracy, the ambient temperature derivable from the isothermal preliminary period, and to check the K value.

If the scatter of the K values found independently of each other is $< \pm 3\%$, the mean value $\bar{K}$ may be used for the evaluation of the temperature–time curve of the experiment. The last criterion is that $\Delta T(t)$ upon subtraction of $\Delta T_{\mathrm{corr}}(t)$ from $\Delta T_{\mathrm{exp}}(t)$ must not show any systematic trend in the after-period. The variation in $\Delta T(t)$ must be smaller than $\pm 1\%$ within the entire after-period. With this condition it will be possible to obtain, near saturation concentration, easily reproducible results for $\Delta_{\mathrm{s}} H_{\mathrm{b}} = f(m_{\mathrm{b}})$ even for salts whose dissolution periods are > 60 min under optimum agitation conditions.

RESULTS AND DISCUSSION

$\Delta_s H_b = f(m_b)$ was determined experimentally for the salts KCl, KBr, KI, NH_4Cl, NH_4Br and RbCl. The results of the investigations are shown in Figs. 1 and 2. By extrapolation of the calculated regression line with respect to $m_b = m_{b,sa}$, $\Delta_s H_{b,sa} = -\Delta_c H_b$ is determined. Table 1 lists the enthalpies of crystallization found in this way for the salts investigated. To evaluate the reliability of the results, the possible sources of error were analyzed. It was found that analyzing, weighing and calibration errors are negligible. The decisive factors are the influence of substance-specific properties, especially of the rate of dissolution and the reliability of establishing the dissolution equilibrium, on the quality of evaluation of the curves obtained by measurement. The computational evaluation of the curves has shown that, for the dissolution of KCl, KBr and KI in nearly saturated solutions, 90 min were required for establishing the equilibrium under optimum conditions of agitation, whereas only about 45 min were required for the dissolution of NH_4Cl, NH_4Br and RbCl. Taking into account the uncertainties occurring in the determination of K and T_a, the errors specified in Table 1 should be justified.

Evaluation of the effect of changes in concentration ($\Delta m < 1\%$) on the

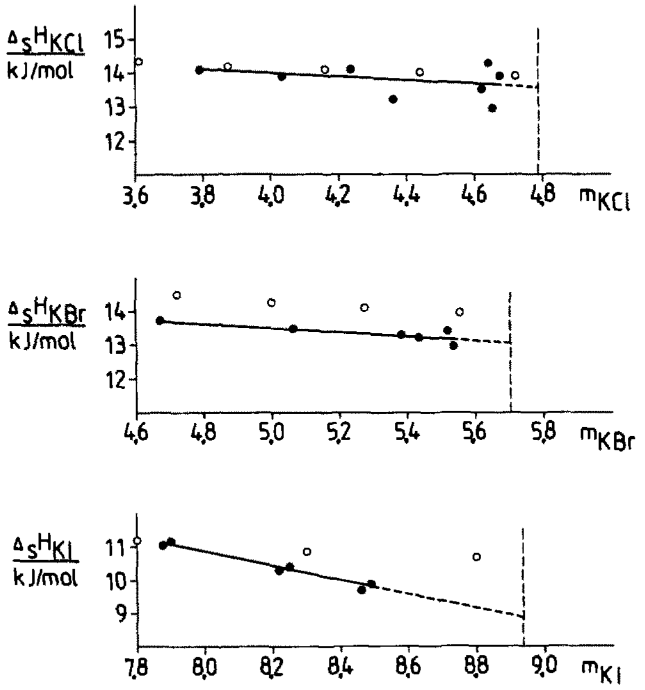

Fig. 1. Partial molar enthalpies of solution $\Delta_s H_b$ of b = KCl, KBr and KI depending on the molality m_b of the solution at 298.15 K: ● our values; ○ values from ref. 15.

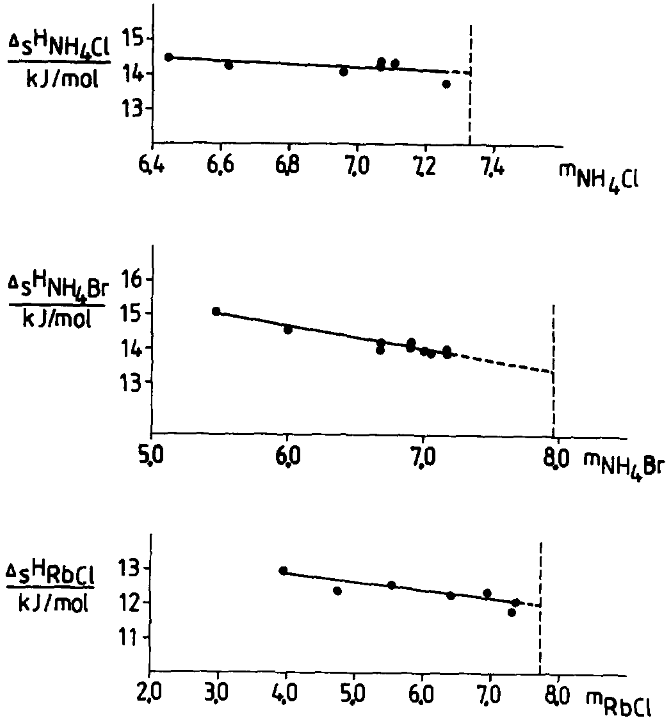

Fig. 2. Partial molar enthalpies of solution $\Delta_s H_b$ of b = NH_4Cl, NH_4Br and RbCl depending on the molality m_b of the solution at 298.15 K.

partial molar enthalpy of solution allows us to state that the change in the partial molar enthalpies of salt and water in the solution is negligibly small compared with the partial molar enthalpies of solution measured.

A comparison of the results (Table 1) with corresponding values reported elsewhere (Table 2) is predicative to a limited extent. The values given for $\Delta_c H_b$ in the literature and determined experimentally or by calculation according to widely differing methods show satisfactory agreement only in

TABLE 1

Enthalpies of crystallization $\Delta_c H_b$ of salts determined at 298.15 K from the function $\Delta_s H_b = f(m_b)$

Salt	$\Delta_c H_b$	Estimated error $\Delta(\Delta_c H_b)$ (%)
KCl	−13.6	10
KBr	−13.0	10
KI	−8.9	10
NH_4Cl	−14.1	5
NH_4Br	−13.5	5
RbCl	−12.0	5

TABLE 2

Bibliographical data on the enthalpy of crystallization $\Delta_c H_b$ of the salts investigated at 298.15 K

Salt	$\Delta_c H_b$ (kJ mol^{-1})			
	Measured directly	From $\Delta_s H_b = f(m_b)$	From $\Delta_s^{in} H_b$	Calculated
KCl	-13.62 [10]	-13.85 [5]	-13.93 [1]	-14.09 [19]
	-13.55 [13]	-13.86 [15]	-13.68 [9]	-13.39 [10]
	-14.34 [13]		-13.22 [17]	-14.01 [11]
	-14.40 [13]		-13.61 [11]	-14.15 [20]
	-13.79 [14]			-13.85 [21]
KBr	-14.13 [10]	-13.87 [15]	-13.51 [1]	-14.17 [19]
	-14.56 [13]		-13.7 [9]	-13.93 [10]
	-14.53 [13]		-13.43 [17]	-13.98 [11]
	-13.46 [13]		-13.54 [11]	-13.91 [3]
			-13.93 [18]	
KI		-10.89 [15]	-9.15 [1]	-9.15 [19]
			-10.5 [9]	-11.15 [21]
			-10.1 [17]	-9.4 [11]
NH_4Cl		-14.0 [16]		-18.4 [22]
				-16.24 [21]
NH_4Br				-15.12 [21]
RbCl				-11.74 [22]
				-10.66 [10]
				-12.18 [21]

exceptional cases. The reasons for this are the problems entailed by the investigation of nearly saturated solutions and those inherent in the methods used [6]. Hence, correspondence of the initial data for calculations of $\Delta_c H_b$ is also poor.

Table 2 shows that $\Delta_c H_b$ values for KCl, which have been determined by experiment or calculation, scatter around a mean value of $\Delta_c \overline{H}(\mathrm{KCl}) = -13.75$ kJ mol^{-1} by ±2%, apart from a few values which deviate to a greater extent. That the value obtained by us lies within the spread could be considered as evidence of the reliability of our method of measurement. This is borne out by a comparison of the experimental results for NH_4Cl. The greater deviation of the calculated values (Table 2) observed in this case should point to incorrect initial data for the calculation. For NH_4Br and RbCl, the reason for the deviation of the calculated literature values from our measured values should be the same. An appropriate comparison of the $\Delta_c H_b$ values of KBr of KI shows that the values measured by us are lower by 6 and 12%, respectively, than the mean value of the data from the literature. Moreover, it should be taken into account that the literature values for KBr and KI scatter around this mean value by ±4 and ±10%, respectively. It is not possible to evaluate these results.

Because of the importance of the $\Delta_c H_b$ values, a critical analysis of known values is necessary. However, the considerable differences observed in the results suggest that calorimetric-methodical problems probably are not the cause. Results in better agreement will be obtained only be comprehensive valuation and consideration of substance-specific properties.

The method presented herein for the experimental determination of $\Delta_c H_b$ appears to be reliable and is used for studying the effect of foreign salts on $\Delta_c H_b$ [23].

REFERENCES

1 H.-H. Emons, G. Wolf and C. Kropp, Thermochim. Acta, 81 (1984) 59.
2 R. Rychly, Chem. prumsl., 24 (1974) 446.
3 R. Rychly, Krist. Tech., 10 (1975) K 91–K 93.
4 R. Rychly and V. Pekárek, J. Chem. Thermodyn., 9 (1977) 391.
5 J. Nývlt, Industrial Crystallization. The Present State of the Art, Verlag Chemie, Weinheim, 1978.
6 S. Kolarik, V. Pekárek and V. Vacek, Chem. prumsl., 32 (1982) 516
7 V. Vacek and A. König, Thermochim. Acta, 70 (1983) 225.
8 N. Beketov, Bl. Akad. Petersb., 34 (1892) 292.
9 V.B. Parker, Thermal Properties of Aqueous Univalent Electrolytes, NSRDS-NBS-2, U.S. Government Printing Office, Washington, 1965.
10 H. Nakayama, Bull. Fac. Eng., Yokohama Natl. Univ., 19 (1970) 29.
11 R.A. Robinson and R.H. Stokes, Electrolyte Solutions, Butterworths, London, 1959.
12 I. Wadsö, Sc. Tools, 13 (1966) 33.
13 A. Glasna and M. Tassa, Isr. J. Chem., 12 (1974) 799.
14 F.L. Shibita, S. Oda and S. Furukova, J. Sci. Hiroshima Univ., 1 (1931) 55.
15 J. Wüst and E. Lange, Z. Phys. Chem., 116 (1925) 161.
16 K.P. Mishchenko and G.M. Poltoratski, Termodinamika i stroenie vodnykh i nevodnykh rastvorov elektrolitov, Khimiya, Leningrad, 1976.
17 G.R. Alakhverdov, B.D. Stepin and N.I. Sorokin, Kristallisatsiya, 2 (1976) 111.
18 H. Hammerschmid and A.L. Robinson, J. Am. Chem. Soc., 54 (1932) 3120.
19 A.N. Kirgintsev and A.V. Lukyanov, Zh. Neorg. Khim., 12 (1967) 2032.
20 A.T. Williamson, Trans. Faraday Soc., 40 (1944) 421.
21 I.E. Vozkresenskaya, Razshirennye tablici koefficientov vodnykh rastvorov 150 elektrolitov pri 25°C, voprosy fiziceskoj khimii rastvorov elektrolitov, Khimya, Leningrad, 1968.
22 A.N. Kirgintsev, Zh. Fiz. Khim., 39 (1965) 177.
23 H.-H. Emons, G. Wolf and C. Kropp, to be published.