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ENTHALPIES OF CRYSTALLIZATION OF HALOGENIDES. PART 1. INVESTIGATIONS OF THE ENTHALPIES OF CRYSTALLIZATION OF SALTS AT 298.15 K FROM THE WHOLE ENTHALPY OF DISSOLUTION

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ABSTRACT

Published methods to determine enthalpies of crystallization of salts from aqueous solutions are critically reviewed. An indirect method for the experimental determination of the enthalpy of crystallization using a new method to measuring the whole enthalpy of dissolution is presented. First results for NaCl, $KF \cdot 2\ H_2O$, KCl, KBr and KI are compared with published data.

INTRODUCTION

The molar enthalpy of crystallization, $\Delta_c H_b$, the change of the enthalpy at the transition of one mole of a salt b from the saturated solution to the solid, crystalline state is a value of high scientific and technological importance. $\Delta_c H_b$ corresponds to the negative value of the partial molar enthalpy of dissolution, $\Delta_s H_b$, of the salt b at the limiting case of the saturated solution and is often called the last molar enthalpy of dissolution of the substance b

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

The numerical value of $\Delta_c H_b$ is determined by the difference between the enthalpy of formation and the partial molar enthalpy of the salt in the saturated solution.

The general connection between the partial molar enthalpy of dissolution, $\Delta_s H_b$, and the integral molar enthalpy of dissolution, $\Delta_s H_{b,in}$, of the substance b and the integral dissolution enthalpy, $\Delta_s h_{in}$, respectively

$$\Delta_s H_{b,in} = \frac{\Delta_s h_{in}}{n_b} = \frac{n_a}{n_b} \Delta_D H_a + \Delta_s H_b \tag{2}$$

(where $\Delta_D H_a$ is the partial molar enthalpy of dilution of the solvent a) is

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applicable to the limiting case $m = m_{sa}$ (where m = molality of the solution, and n_i = number of moles of the component i)

$$(\partial_s h_{in}/\partial n_b) = \Delta_s H_{b,sa} = -\Delta_c H_b\langle m = m_{sa}\rangle \tag{3}$$

The enthalpy of crystallization includes information about the state of the dissolved substance in the saturated solution, the solid phase being dissolved in the solution, and about the change of these values due to the influence of foreign salts or by partial or whole substitution of the aqueous solvent. Integral and partial statements about the process of crystallization, frequently used in chemical technology for separation, can also be obtained; thermokinetic investigations, investigations of the formation of crystal nuclei and crystal growth use the heat of crystallization as an indicator.

In contrast to these versatile and important applications, only few reliable values of the enthalpy of crystallization are known for simple systems (mostly aqueous solutions) from the methods available for their direct or indirect experimental or mathematical determination.

In direct measurements of the crystallization enthalpy the heat exchange on crystallization from the supersaturated solution due to the transition of the solution to the saturated state is investigated. Results from such measurements are not very reliable because of the undefined initial state (supersaturated solution), the questionability of the definition of the equilibrium after crystallization and the inaccuracy of the determination of the amount of crystallized substance. Results from investigations with this method are published in refs. 1 and 2.

In the indirect experimental determination of the enthalpy of crystallization, two methods are distinguishable. $\Delta_c H_b$ can be determined by the pseudo-partial molar enthalpy of dissolution of b (eqn. 1), or from the integral enthalpy of dissolution, $\Delta_s h_{in}$ (eqn. 3). By using the first method the dependence of $\Delta_s H_b$ on the ratio m/m_{sa} near the saturation concentration is experimentally determined by dissolving milligram amounts of b are in the approximately 10^3-fold amount of the nearly saturated solution (change of molality at the experiment $< 3\%$). The exchanged heat corresponds to the pseudo-partial molar enthalpy of dissolution, $\Delta_s H_b$. Using eqn. (1) we can obtain the enthalpy of crystallization by extrapolation of $\Delta_s H_b(m)$ to $m = m_{sa}$. Although gratifying results are achieved with this method [2–5], there are varied experimental problems due to the relatively small thermal effects and the very slow velocity of the dissolution. Even in the second indirect experimental method, in which the quantity of the thermal effect can be adequately chosen for the measuring equipment used, the slow dissolving process near the saturation is a decisive source of errors. The accuracy of the results of the integral enthalpy of dissolution measured up to the saturation point are mostly insufficient for the determination of $\Delta_c H_b$ with high precision by the first derivative (eqn. 3). Results of corresponding investigations are communicated in refs. 6–8.

Calculations of the enthalpy of crystallization from the temperature coefficient of the solubility, the coefficient of activity and the osmotic coefficient [3,7,9–12], are also of very limited reliability because the initial data mentioned often differ considerably. This may be caused by the easily possible formation of states of non-equilibrium (e.g., supersaturation).

A detailed survey of several methods of determining $\Delta_c H_b$ including appreciation is given in ref. 6. Problems of the calculation of $\Delta_c H_b$ are discussed in ref. 12.

In the framework of this paper a modified indirect method of experimental determination of the enthalpy of crystallization is presented and tested by measuring $\Delta_c H_b$ for various salts. The enthalpy of crystallization is obtained in the form of $-\Delta_s H_b$ for $m = m_{sa}$ from the integral enthalpy of dissolution $\Delta_s H_{b,in}$ and the partial molar enthalpy of dilution $\Delta_D H_a$ (eqn. 2). $\Delta_s H_{b,in}$ $(m = m_{sa})$ is measured directly by adding a few grams of solvent (solvent a) through an ampoule or titrating apparatus to the calorimeter cell, in which about 80 ml of saturated solution plus solid phase have been stirred. Thereby the calorimetrically effective state change consists of the formation of a saturated solution, which is proportional to the amount of solvent added. In the ampoule technique the moles of dissolved salt are determined by means of known solubility data and, in the titration technique, by means of the entire amount of added solvent necessary for the dissolution of the whole solid phase.

This method of determining $\Delta_s H_{b,in}$ $(m = m_b)$ was tested because it promised the following advantages. The integral value is determined in one step with an optimally adaptable thermal effect for the available calorimeter. The state of salt in the solid phase can be determined with a high reliability. The experiment results in a saturated solution with a high probability and an acceptable velocity. $\Delta_D H_a$ at $m = m_{sa}$ is determined in terms of a pseudo-partial molar enthalpy of dilution. Very small amounts of solvents (a few mg) are added to ~ 80 ml of a nearly saturated solution of different concentrations, and $\Delta_D H_a$ $(m = m_{sa})$ is investigated by extrapolation of the results.

EXPERIMENTAL

All calorimetric investigations presented in this paper were carried out with a modified LKB calorimeter (model 8700) at $T = 298.15$ K and with aqueous solutions. For measuring the integral enthalpy of dissolution of the salt b, 80 ml of the saturated solution were placed in the calorimetric cell together with a few grams of the salt as deposit. By means of an ampoule technique, up to 3 g of water could be added as the solvent to start the calorimetric experiment. The water dissolves the salt from the solid phase up to saturation point. In this process the amount of saturated solution formed is proportional to the amount of water added. The isoperibol mode of operation of the calorimeter indicates the exchanged heat in terms of a change in temperature, which can be recorded analogically or digitally. The heat capacity of the measuring systems is determined by an electric heating experiment. The calculation of the measuring data recorded can be carried out by means of a computer.

For determining the partial molar enthalpy of dilution, the pseudo-differential method was used. An 80-ml sample of the nearly-saturated solution was placed in the cell and—in the calorimetric experiment proper—diluted with such a small amount of solvent that, apparently, no change of molality ($\Delta m < 1\%$) takes place. The addition of maximally, 500 mg of solvent (on average 100 mg) was made either by an ampoule technique or with a micro-burette. The titration technique proved favourable, especially for endothermic dilution effects, because a great number of measurements could be carried out in a rapid succession by alternating experiments of dilution and electrical heating. The registration and analysis of data was carried out as for the dissolution experiments. By investigating solutions of different molality and through extrapolation, $\Delta_D H_a$ for $m = m_{sa}$ could be determined.

For the following salts the enthalpy of crystallization from water was determined by experiments of dissolution and dilution.

Salt	Quality	Molar weight	Solubility at 298.15 K (g salt/g free water)
NaCl	pure	58.443	0.3596
$KF \cdot 2\,H_2O$	pro analysi	94.127	4.363
KCl	pro analysi	74.551	0.3569
KBr	pro analysi	119.002	0.6786
KI	purest	166.002	1.4821

The salts used were additionally purified by recrystallizing the salt twice by means of bidistilled water.

RESULTS AND DISCUSSION

To determine the change of enthalpy, Δh, associated with the investigated change of state, ΔT has to be determined initially from the temperature–time curve recorded. The correction necessary for the exchange of heat of the calorimeter with the surroundings can be made by means of the computer. From the ΔT value and the result of the calibration, Δh is obtained in the usual way.

For calculating the integral molar enthalpy of dissolution, $\Delta_s H_{b,in}$, of substance b the number of moles, n_b, of the dissolved substance b (eqn. 2) needs to be known. Owing to the non-isothermal operation manner of the calorimeter, n_b is the sum of two contributions, n'_b and n''_b. The addition of water to the solid phase–saturated solution system effects the dissolution of b, proportionally to the amount of water, m_a, added in the calorimetric experiment. The proportionality factor is the solubility, $l_{b,T}$, of b in solvent a at temperature T_A at the beginning of the calorimetric after-period and, thus, at the end of saturation of the water added

$$n'_b = l_{b,T_A} m_a \tag{4}$$

The second contribution, n''_b, follows directly from the change in temperature in the measuring system resulting from the dissolution process and the change of the solubility dependence on temperature. The value of n''_b can be calculated from the temperature coefficient of solubility, l'_T, the temperature-difference, $T_A - T_B$ (T_B equates to the temperature at the end of the preliminary period), and the whole amount of solvent, w_a, in the calorimetric cell:

$$n''_b = l'_T (T_A - T_B) w_a \tag{5}$$

For $\Delta_s H_{b,in}$, the following is obtained

$$\Delta_s H_{b,in} = \Delta h \left[l_T m_a + l'_T (T_A - T_B) w_a \right]^{-1} \tag{6}$$

The necessary information on the solubility of the investigated salts was taken from ref. 13. The values of $\Delta_s H_{b,in}$ calculated according to eqn. (6) for saturated solutions ($m = m_{sa}$) are given in Table 1 together with results from the literature. The values given in this table are average values from at least five separate measurements.

The partial molar enthalpies of dilution, $\Delta_D H_a$, were determined by the calorimetric experiments described. For extrapolation to determine $\Delta_D H_a$ at $m = m_{sa}$ at least five measurements with different values of m, nearly m_{sa} ($m/m_{sa} > 0.7$), were always carried out. The results of the investigations are given in Table 2 together with data from the literature.

On the basis of the results communicated in Tables 1 and 2 the molar enthalpies of crystallization, $\Delta_c H_b$, for the investigated salts were determined by applying eqn. (2). These results are given in Table 3, in comparison with data from the literature.

TABLE 1

Integral enthalpy of dissolution, $\Delta_s H_{b,in}$ (kJ mol^{-1}), of the salt b in water at $m = m_{sa}$ and $T = 298.15$ K

Salt b	This work	Literature
NaCl	1.82	1.87 [14,15]
$KF \cdot 2\,H_2O$	14.73	14.63 [16]
KCl	15.52	15.46 [14] 15.44 [17]
KBr	16.09	16.50 [14]
KI	12.37	14.08 [14]

A comparison of the method described for an investigation of the molar enthalpy of crystallization is only possible by comparing the accidental errors of different methods. Only the reliability of the reproducibility of different methods can be used as a basis for their appreciation. Standard or basic values for enthalpies of crystallization are unknown.

A critical regard of the experimental and calculation methods mentioned for the determination of the enthalpy of crystallization, results in the following conclusions in accordance with ref. 6. At present, direct measurements of the enthalpy of crystallization by spontaneous or artificial crystallization from a supersaturated or supercooled state probably provide results

TABLE 2

Partial molar enthalpy of dilution, $\Delta_D H_a$ (J mol^{-1} H_2O), for saturated solutions ($m = m_{sa}$) with the solvent water at $T = 298.15$ K

Salt b	This work	Literature
NaCl	39.8	34.1 [14]
$KF \cdot 2\,H_2O$	−2900	−2850 [16]
KCl	136.9	144 [14]
KBr	265.7	247 [18]
		270 [14]
KI	518.8	515.8 [14]

TABLE 3

Molar enthalpy of crystallization, $\Delta_c H_b$ (kJ mol^{-1}), of the salt b at $T = 298.15$ K compared with literature values, which were measured by different methods

Salt b	This work	Literature values			
		Directly measured	From $\Delta_s H_b$	From $\Delta_s H_{b,in}$	Calculated
NaCl	−1.46		−1.51 [19]		−1.54 [19]
$KF \cdot 2\,H_2O$	−18.20		−18.15 [20]	−25.2 [5]	−20.64 [21]
				−24.5 [22]	
KCl	−13.93	−13.62 [3]	−13.85 [20]	−14.07 [20]	−14.09 [11]
		−13.55 [1]		−13.68 [5]	−13.39 [3]
		−14.34 [1]		−13.22 [8]	−14.01 [7]
		−14.40 [1]		−13.61 [7]	−14.13 [9]
		−13.77 [16]			−13.85 [21]
		−13.85 [13]			
		−13.79 [22]			
KBr	−13.51	−14.13 [3]		−13.7 [5]	−14.17 [11]
		−14.56 [1]		−13.43 [8]	−13.93 [3]
		−14.53 [1]		−13.54 [7]	−13.98 [7]
		−13.46 [1]		−13.93 [18]	−19.91 [19]
KI	−9.15			−10.5 [5]	−9.15 [11]
				−10.1 [8]	−9.4 [7]
				−10.5 [20]	−11.15 [21]

with the greatest accidental error. Difficulties in determining the amount of crystallized salt and in defining the initial and final states are reasons of the range of errors up to ±15%. By using experimental investigations of integral enthalpy of dissolution for determining $\Delta_c H_b$ an uncertainty of the results of 2–10% is to be expected. The mentioned range also seems to be suitable to all calculating methods for determining $\Delta_c H_b$. Only by means of very precise measurements of the pseudo-partial molar enthalpy of dissolution [6] the reproducibility of the results for $\Delta_c H_b$ should be > 2 or 3%. In this method, too, the attainable accuracy also depends considerably on the investigated system.

The accuracy of enthalpies of crystallization determined in this study (Table 3) is only dependent on the results of measurements of the integral enthalpy of dissolution. The necessary determinations of the enthalpy of dilution could be carried out so precisely that the uncertainty is < 0.5%. In contrast, the dispersion of results for $\Delta_L H_{b,in}$ of KBr and KI (Table 1) reaches nearly ±5%. For KCl, and especially for NaCl, this value amounts to ±2 and ±1%, respectively. Since in each case at least five measurements with very different additions of water ($0.3\ g \leqslant m_a \leqslant 3\ g$) and therefore different ΔT values, for determining a $\Delta_s H_{b,in}$ value were carried out and because the temperature coefficient of solubility, l_T, in water is very different for the substance investigated, specific properties of the substances are regarded as an essential reason of the dispersion of $\Delta_s H_{b,in}$ and, therefore, $\Delta_c H_b$. The speed and reliability of the establishment of equilibrium near saturation are very different for aqueous solutions of a number of salts and should be a decisive factor of the reliability of the experimental methods for ascertaining $\Delta_c H_b$.

In summing up, we can say that the results for $\Delta_c H_b$ (Table 3), $\Delta_s H_{b,in}$ (Table 1) and $\Delta_D H_a$ (Table 2) obtained by means of the method described are in good agreement with the most probable values, which are well-known from the literature. The reliability of the results for $\Delta_c H_b$ is better than that of the values obtained from the first derivation of the concentration dependence of $\Delta_s H_{b,in}$, and can be compared with the results of investigations of the pseudo-partial molar enthalpy. On the other hand, however, the method introduced seems to be less expansive in experiments.

An improvement of the reliability of results of investigations of enthalpy of crystallization could probably be achieved by used of higher measuring temperatures. The resulting kinetic advantages should outweigh the uncertainty in calculating back to 298.15 K.

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