

## HEATS OF CRYSTALLIZATION OF POTASSIUM CHLORIDE AND MAGNESIUM CHLORIDE HEXAHYDRATE FROM AQUEOUS SOLUTIONS AT 298.15 K. A CRITICAL REVIEW

VÁCLAV VACEK

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

AXEL KÖNIG

*Sektion Chemie, Bergakademie Freiberg, 9 200 Freiberg (D.D.R.)*

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### ABSTRACT

Published data on the heats of crystallization from aqueous solutions of potassium chloride and magnesium chloride hexahydrate are critically reviewed and compared with those evaluated from solubility and activity data. The recommended values of the heats of crystallization are  $-13.8 \pm 0.1$  kJ mole<sup>-1</sup> for KCl and  $-15.8_{\pm 2.8}^{-0.3}$  kJ mole<sup>-1</sup> for MgCl<sub>2</sub>·6 H<sub>2</sub>O. A test of the mutual consistency of data for dissolution heats, temperature dependence of solubility and concentration dependence of activity and/or osmotic coefficient is a side-issue of the review.

### INTRODUCTION

In contrast to the extensive literature on the properties of dilute aqueous solutions of highly soluble inorganic salts, very little information is available on the properties at concentrations near saturation. Heats of crystallization of common inorganic salts can be useful not only for energy balances in industrial crystallization processes, but also as thermodynamic characteristics related to a number of other physico-chemical quantities of saturated solutions. The aim of this paper is to summarize the present state of knowledge on the heats of crystallization of KCl and MgCl<sub>2</sub>·6 H<sub>2</sub>O from their aqueous solutions at 25°C. Crystallization heats obtained from solubility and activity data are compared with those evaluated from integral and differential dissolution heats, and with heats of crystallization previously published and critically compiled by us. For completeness, empirical correlations proposed for the heat of crystallization,  $\Delta H_c$ , are also examined.

## LITERATURE REVIEW

Williamson's pioneering analysis [1] of the calculation of the heat of crystallization from solubility and activity data included the system  $\text{KCl-H}_2\text{O}$ , for which previously measured values were also summarised [1]. The value was recalculated independently by Kirgintsev [2] and Kirgintsev and Lukyanov [3], who also considered the system  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O-H}_2\text{O}$ . Crystallization heats of both these salts have been included also in Nakayama's review [4], where data evaluated from solubility and activity data are compared with measured values of the last differential heat of dissolution.

Allakhverdov et al. [10] have evaluated  $\Delta H_c$  for  $\text{KCl-H}_2\text{O}$  from integral heats of dissolution given in Parker's compilation [17].

Directly measured values of crystallization heats (i.e. from the thermal effects of crystallization under well-defined conditions) are extremely rare in the literature. No such values for potassium and/or magnesium chloride at  $25^\circ\text{C}$  have been found. Glasner and Kenat [19] have reported a value of  $\Delta H_c$  for  $\text{KCl-H}_2\text{O}$  at  $35^\circ\text{C}$  (see also ref. 7). Rychlý and Nývlt [7], Rychlý [8] and Nývlt [9] have presented a compilation of some published heats of crystallization of inorganic salts from their aqueous solutions, including  $\text{KCl}$  and  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ . Extensive experimental results of differential heats of dissolution including the case of  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  have been published by Tsvetkov and Tsvetkov [6]. A systematic critical compilation of the heats of crystallization for selected potassium salts from their aqueous solutions has been given in a series of papers [20–25].

## METHODS OF DATA EVALUATION

The relationships which have been used to evaluate heats of crystallization [1,4,10,20] are summarised in Table 1, where semi-empirical relations proposed for the estimation of  $\Delta H_c$  are also included.

The most direct relation between the heat of crystallization and the differential heat of dissolution, e.g. eqn. (1), can only be applied to differential heats of dissolution measured sufficiently close to saturation concentration with the desired degree of precision. The standard compilation monograph [27] on dissolution heats includes only one set of such data for the  $\text{KCl-H}_2\text{O}$  system given by Wust and Lange [28]. The few points far from the saturation concentration given for  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  in crude graphical form [6] (see Fig. 2 in ref. 6) provide a value of the last differential heat of dissolution of  $10.5 \text{ kJ mole}^{-1}$  with uncertain experimental error. With the exception of Nakayama's experimental value [4,5] of  $11.92 \text{ kJ mole}^{-1}$ , also evaluated from differential heats of dissolution, no further measured value has been found in the literature for this salt. For comparison, all values

TABLE 1

Relations for  $\Delta H_c$  evaluation

$$\Delta H_c = - \lim_{m \rightarrow m_s} \Delta L(m) \equiv - \Delta L(m_s) \quad (1)$$

$$\Delta L(m) = \frac{\partial}{\partial m} [m \Delta H(m)] = \Delta H(m) + m \frac{d\Delta H(m)}{dm} \quad (2)$$

$$\Delta H_c = - \Delta L(m_s) = - [\Delta H^0 + \bar{L}_2(m_s)] \quad (3)$$

$$\Delta H^0 = \lim_{m \rightarrow 0} \Delta H(m) \quad (4)$$

$$\bar{L}_1 = - \frac{M_1 m^2}{1000} \frac{\partial \phi_L}{\partial m} \quad \bar{L}_2 = \frac{\partial}{\partial m} [m \phi_L(m)] \quad (5)$$

$$\phi_L = \Delta H(m) - \Delta H^0 \quad (6)$$

$$- \Delta H_c = \Delta L(m_s) = PRQW \quad (7)$$

$$P = 1 - n m_s / K; \quad Q = d \ln m_s / d(1/T)$$

$$W = \nu \left[ 1 + \left. \frac{d \ln \gamma_{\pm}}{d \ln m} \right|_{m_s} \right] \quad (8a)$$

$$= \nu \frac{\partial}{\partial m} (m \phi)_{m_s} = \nu \left[ \phi + m \frac{\partial \phi}{\partial m} \right]_{m_s} \quad (8b)$$

$$= -K \left. \frac{\partial \ln a_w}{\partial m} \right|_{m_s} \quad (8c)$$

compiled and/or evaluated here are summarised in Table 2.

The derivative of the concentration dependence of the integral heats of dissolution can also be used to evaluate the heat of crystallization. The data in integral form are available for a number of systems (see, for example, refs. 17 and 27). However, the differentiation and subsequent extrapolation according to eqns. (1) and (2) usually increase considerably the uncertainty of a few per cent in the experimental points for the concentration dependence of integral heat of dissolution,  $\Delta H(m)$ .

Values of  $\Delta H_c$  evaluated from dissolution heats taken from Parker's [17] and Beggerow's [27] recent review for the KCl-H<sub>2</sub>O system are given in Table 2A. Molecular weights of compounds were taken from the IUPAC 1971 recommendation [15], i.e.  $M_w = 18.0153$ ,  $M_{KCl} = 74.551$ ,  $M_{MgCl_2} = 95.1202$ . Extrapolation and/or interpolation procedures were repeated for 4-8 points of the concentration dependence near saturation. The points were fitted by the method of maximum likelihood to three types of parabola

$$g(m) = \sum_{i=1}^3 a_i m^{(i-1)/2}$$

$$g(m) = \sum_{i=1}^3 b_i m^i$$

TABLE 2

Summary of published and evaluated heats of crystallization,  $-\Delta H_c$  (kJ mole<sup>-1</sup>)  
A. KCl-H<sub>2</sub>O system.

| From solubilities eqn. (7) | Refs. for term |     | From integral heats of dissolution, eqns. (1), and (2) | Ref. | From differential heats of dissolution, eqn. (1) | Ref. |
|----------------------------|----------------|-----|--|------|--|------|
|                            | $Q$            | $W$ |  |      |  |      |
| 14.02                      | 3              | 3   | 14.07  | 27   | 13.85  | 27   |
| 13.56                      | 4              | 4   | 13.68  | 17   | 13.85  | 28   |
| 14.01                      | 15             | 13  | 13.22  | 10   | 13.79  | 36   |
| 14.13                      | 1              | 1   |  |      | 13.77  | 37   |
| 13.85                      | 15             | 16  |  |      |  |      |
| 13.77                      | 12             | 11  |  |      |  |      |

Recommended value of  $\Delta H_c = -13.8 \pm 0.1$  kJ mole<sup>-1</sup>

B. MgCl<sub>2</sub>·6 H<sub>2</sub>O-H<sub>2</sub>O system

| From solubilities eqn. (7) | Reference for term |     |     | From differential heats of dissolution eqn. (1) | Ref. |
|----------------------------|--------------------|-----|-----|---|------|
|                            | $m_s$              | $Q$ | $W$ |   |      |
| 11.05                      | 4                  | 4   | 4   | 11.92   | 4    |
| 13.04                      | 3                  | 3   | 3   | 10.5  | 6    |
| 13.02                      | 38                 | 15  | 16  |   |      |
| 16.03                      | 34                 | 35  | 34  |   |      |
| 15.7                       | 35                 | 35  | 34  |   |      |

Recommended value for  $\Delta H_c = -15.8_{+2.8}^{-0.3}$  kJ mole<sup>-1</sup>

$$\ln g(m) = \sum_{i=1}^3 c_i (\ln m)^{i-1}$$

The mean  $g(m_s)$  evaluated from all cases, i.e. from 4, 5, ... 8 points fitting, was used as the value sought, while the maximum difference of these values was used as an estimated error of an extrapolation or interpolation procedure. Integral heats of dissolution were calculated from eqn. (7) using data on the integral heat of dilution or apparent molal heat content of a solution taken from ref. 17. Dissolution is an exothermic process in certain cases, but an endothermic one in others. Following the accepted convention, e.g. by the Landolf-Börnstein tables [27], we take endothermic dissolution heats as positive; to the contrary crystallization of KCl and MgCl<sub>2</sub>·6 H<sub>2</sub>O is exothermic, i.e.  $\Delta H_c < 0$ . A rigorous relation between temperature dependence of solubility,  $d \ln m_s / d(1/T)$  and the heat of crystallization has been known for a long time [1,4]. A program of systematic evaluation of crystallization heats according to eqn. (7) was suggested by Williamson [1] 40 years ago. Nakayama [4] and Kirgintsev and Lukyanov [3] are the only authors

that have used this advantageous method to any great extent for the evaluation of  $\Delta H_c$ , namely for 35 and 70 binary inorganic systems, respectively. Their results for KCl [1,3,4] and for  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  [3,4] are summarised in Table 2 together with values calculated in the present work.

A universal strategy for determining the best value is simply to use the best experimental data for its evaluation. The best available data on solubilities are probably those given in recent critical reviews by Potter and Clyne [12] for KCl and by Clyne and Potter [35] for  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ . The latest data of Hamer and Wu [11] on osmotic and activity coefficients for KCl, and those given for  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  system by Rard and Miller [34] were used. In order to show how the resulting  $\Delta H_c$  evaluated from eqn. (7) is sensitive to the quality of the input data, we also present in Table 2 a few results evaluated from data taken from standard reference books [13–17]. The data were treated using the same extrapolation or interpolation procedure as mentioned above. The resulting values of the terms  $Q$  and  $W$  of eqn. (7) are summarised in Table 3. Equations used for the calculation of  $Q$  and  $W$  are summarised in Table 4, where empirical correlations proposed by Nakayama [4], Aizin et al. [18], and Rychlý and Nývlt [7] (see also Nývlt [9]) for  $\Delta H_c$  are also included.

TABLE 3

Thermodynamic characteristics used to evaluate  $\Delta H_c$  from temperature dependence of solubility and concentration dependence of activity and/or osmotic coefficients at 25°C

A. KCl–H<sub>2</sub>O system

| $m_s$ | Ref. | $Q$   | Ref. | $W$   | Ref. | $-\Delta H_c$ | Ref. |
|-------|------|-------|------|-------|------|---------------|------|
| 4.82  | 3    | 736.9 | 3    | 2.30  | 3    | 14.02         | 3    |
| 4.81  | 4    | 725   | 4    | 2.25  | 4    | 13.56         | 4    |
| 4.808 | 1    | 739.6 | 1    | 2.298 | 1    | 14.13         | 1    |
| 4.76  | 15   | 747.9 | 15   | 2.253 | 13   | 14.01 ± 0.02  | TW   |
| 4.83  | 16   | 747.9 | 15   | 2.227 | 16   | 13.85 ± 0.04  | TW   |
| 4.778 | 12   | 722.6 | 12   | 2.291 | 11   | 13.77 ± 0.09  | TW   |

B.  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ –H<sub>2</sub>O system

| $m_s$  | $P$    | Ref. | $Q$   | Ref. | $W$   | Ref. | $-\Delta H_c$ | Ref. |
|--------|--------|------|-------|------|-------|------|---------------|------|
| 5.86   | 0.3666 | 3    | 204.7 | 3    | 20.9  | 3    | 13.04         | 3    |
| 5.786  | 0.3746 | 4    | 196.4 | 4    | 18.06 | 4    | 11.05         | 4    |
| 5.78   | 0.3752 | 15   | 206.2 | 15   | 18.85 | 13   | 12.77         | TW   |
| 5.781  | 0.3751 | 38   | 206.2 | 15   | 20.24 | 13   | 13.02         | TW   |
| 5.84   | 0.3687 | 16   | 206.2 | 15   | 20.6  | 16   | 13.02         | TW   |
| 5.78   | 0.3752 | 15   | 206.2 | 15   | 20.6  | 16   | 13.25         | TW   |
| 5.8101 | 0.3720 | 34   | 239.9 | 35   | 21.68 | 34   | 16.03         | TW   |
| 5.8818 | 0.3642 | 35   | 239.1 | 35   | 21.68 | 34   | 15.70         | TW   |

TW = this work.

TABLE 4

Equations for evaluation of the various thermodynamic quantities used

For the KCl-H<sub>2</sub>O system according to Hamer and Wu [11]

$$\log \gamma_{\pm} = -\frac{A\sqrt{m}}{1+B\sqrt{m}} + \beta m + C m^2 + D m^3 \quad (9)$$

$$\phi = 1 - Z \left\{ \frac{A}{B^3 m} \left[ (1+B\sqrt{m}) - 2Z \log(1+B\sqrt{m}) - (1+B\sqrt{m})^{-1} \right] - \frac{\beta}{2} m - \frac{2C}{3} m^2 - \frac{3D}{4} m^3 \right\} \quad (10)$$

so that

$$\left. \frac{d \ln \gamma_{\pm}}{d \ln m} \right|_{m_s} = m_s Z \left[ -\frac{A}{2\sqrt{m_s}(1+B\sqrt{m_s})^2} + \beta + 2C m_s + 3D m_s^2 \right] \quad (11)$$

$$\left. \frac{d \phi}{d m} \right|_{m_s} = -Z \left\{ \frac{A}{B^3} \left[ m_s^{-2} \left[ 2 \ln(1+B\sqrt{m_s}) - 1 \right] - \frac{B}{2\sqrt{m_s^3}} - \frac{B}{\sqrt{m_s^3} + B m_s^2} + \frac{1+3B\sqrt{m_s}/2}{(m_s + B\sqrt{m_s^3})^2} \right] - \beta/2 - 4C m_s/3 - 9D m_s^2/4 \right\} \quad (12)$$

where

$$\begin{aligned} Z = \ln 10 & & B = 1.296 & & D = -1.954 \times 10^{-4} \\ A = 0.5108 & & C = 3.599 \times 10^{-3} & & \beta = 7 \times 10^{-5} \end{aligned} \quad (13)$$

Temperature dependence of solubilities are given by

$$S = a_1 + a_2 T + a_3 T^2 \text{ in ref. 12} \quad (14)$$

$$\log X = A + B/T + C \log T \text{ in ref. 15} \quad (15)$$

Considering the relations between concentrations  $S$  and  $X$  and molality  $m$ , it holds that

$$Q = -\frac{d \ln m_s}{d(1/T)} = \frac{T^2}{m_s} \frac{d m_s}{dT} = T^2 \frac{100}{100-S} \frac{1}{S} \frac{dS}{dT} \quad (16)$$

and

$$Q = (B - C T) [Z(1 - X)K] \quad \text{where } X = 10^{A+B/T+C \log T} \quad (17)$$

Concentration dependence of integral heats of dissolution of KCl in water at 25°C given by 31 points of function  $\phi_L(m)$  in ref. 17 is represented by

$$\Delta H(m) = 17.228 + 1.741\sqrt{m} - 2.493 m + 0.759\sqrt{m^3} - 0.0775 m^2 \quad (18)$$

Empirical correlations involving  $\Delta H_c$ .

Nakayama [4]

$$\frac{\Delta H_c}{RT} = \nu \ln \frac{\nu m_s}{K + \nu m_s} - \left[ \frac{\Delta H^0}{RT} - \nu \ln K + \nu \ln \gamma_{\pm}(m_s) \cdot m_s \right] \quad (19)$$

Aizin et al. [18]

$$m(t) = C \left( \frac{a+bt}{bT} \right)^{\Delta H_c \frac{b}{\nu R} (a-273b)^{-2}} \exp \left[ -\frac{\Delta H_c}{\nu R (a-273b) T} \right] \quad (20)$$

Rychlý and Nývlt [7]

$$\Delta H_c = 4.576 \frac{\log c(T_2) - \log c(T_1)}{(1/T_2) - (1/T_1)} \quad (21)$$

## DISCUSSION

*The KCl–H<sub>2</sub>O system*

The integral heat of dissolution of KCl in water at infinite dilution is known within an uncertainty of a few tens of J mole<sup>-1</sup> [17,27,32]. Some properties of dilute aqueous solutions of this salt are known to a high degree of accuracy. This permits KCl–H<sub>2</sub>O to be used as a calibration standard in a number of physico-chemical measurements. Yet, no effort has been made to estimate the reliability of the last differential heat of dissolution and/or crystallization of KCl. It appears that published data for the crystallization heat of KCl are subject to an uncertainty of at least 100–200 J mole<sup>-1</sup>.

Kirgintsev's original value [2] of  $\Delta H_c$  differs by more than 11% from that given in his later work [3] and is not considered here. Allakhverdov et al. [10] have reported a value of  $\Delta H_c$  which differs from that evaluated by us using the same input data given by Parker [17]. Their value [10] is included in Table 2A only for completeness.

As pointed out by Williamson [1] 40 years ago, the weakest point of  $\Delta H_c$  evaluation is the uncertainty in the term  $Q$ . Considering the data from Table 3A, this seems to be true even today. The value  $Q = 748$ , derived from a new version [15] of solubility tables [14], remains uncertain. Recent data [12] lead to  $Q = 722.6$ , a value close to Nakayama's estimate of 725 [14] based on an English version [29] of Russian compilations [30]. These tables [30] were also used by Kirgintsev and Lukyanov [3] together with extensive compilation tables [31]. These authors [3] used  $Q = 737$ , in contrast to Kirgintsev's previous paper [2] where  $Q = 648$ .

It may be noted that Nakayama [4] and Kirgintsev and Lukyanov [3] used the same data [13] for the concentration dependence of activity. However, two different tables are given for the KCl–H<sub>2</sub>O system (ref. 13 pp. 476 and 484). This may explain a slight difference in their values for  $W$ ; in addition, Nakayama consistently used eqn. (8a) to evaluate  $W$ , while Kirgintsev and Lukyanov [3] preferred an alternative version given by eqn. (8c). In this work, we use eqn. (8b), which was recommended by Williamson [1] because of its lower sensitivity to experimental uncertainty in the concentration dependence of the colligative properties. In order to check the numerical procedure, both sets of eqns. (9) and (11), (10) and (12) have been used to evaluate  $W$  [26].

It can be seen from Table 2A that, as expected, the values of the heat of crystallization obtained from differential heats of dissolution exhibit the lowest scatter. It appears justifiable to use an average of these values, i.e.  $-13.8 \pm 0.1$  kJ mole<sup>-1</sup> as the most reliable value of  $\Delta H_c$ . The mean of all the values given in the first two columns (with the exception of the Allakhverdov et al. [10] value of 13.22) gives  $-13.89$  kJ mole<sup>-1</sup>, the upper limit of the above range. The last value in the first column in Table 2A,

$-13.77 \text{ kJ mole}^{-1}$ , was calculated from probably the best available data of  $W$  and  $Q$  terms in eqn. (7). It is the close agreement of this value with the above mean value of  $-13.8 \text{ kJ mole}^{-1}$  obtained from the last dissolution heats which supports our conclusion, that  $-13.8 \pm 0.1 \text{ kJ mole}^{-1}$  may be recommended as the best available estimate for  $\Delta H_c$  of KCl.

#### *The $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}-\text{H}_2\text{O}$ system*

It can be seen from Tables 2B and 3B that the data for this system are considerably less consistent and less extensive compared with the previous case. It is interesting that KCl and  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  have nearly the same values of the heat of crystallization, in spite of the fact that the crystal lattice enthalpy of KCl is several times less than that for  $\text{MgCl}_2$  [33]. As mentioned above, the range of experimental error of Tsvetkov and Tsvetkov's [6] value of 10.5 is not known, but may be expected to be large. Nakayama [4,5] measured differential heats of dissolution near saturation for five binary systems; only two points were measured for the  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}-\text{H}_2\text{O}$  system. Assuming that these two points involve the same experimental error as shown in Fig. 1 in ref. 4 for the  $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}-\text{H}_2\text{O}$  system, the extrapolation to saturation concentration of  $\text{MgCl}_2$  would be subject to an uncertainty in  $-\Delta H_c$  of from 10 to 16  $\text{kJ mole}^{-1}$ .

The data presented by Kirgintsev and Lukyanov [3] were evaluated with rounded values of the constants in eqns. (7) and (8c). Therefore, the data have been recalculated using  $R = 8.31441$  and  $K = 55.50837$ , and the factor  $1 \text{ cal} = 4.184 \text{ J}$ . Heats of crystallization obtained here differ by 0.53% for KCl and by 10.47% for  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  (!) from those in ref. 3, and only the recalculated values have been included in Table 2. After this recalculation, values of  $\Delta H_c$  based on ref. 3 and those obtained by our own evaluation using eqn. (7) and data taken from standard monographs [13,15,38] seem to be mutually consistent. Nakayama's [4] value of  $\Delta H_c$  is smaller by 15%. The combined latest data on osmotic or activity coefficients [34] and on the temperature dependence of solubility [35] lead to a considerably higher value of  $-\Delta H_c$  than those previously evaluated. We prefer here to take the value evaluated from the last mentioned data,  $-\Delta H_c = 15.8_{-2.8}^{+0.3} \text{ kJ mole}^{-1}$  as probably the best available estimate of  $\Delta H_c$  for the  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}-\text{H}_2\text{O}$  system. The rather high and unsymmetrical uncertainty interval has been suggested to represent the contents of the Table 2. It has been remarked [35] that " $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$  proved to be the most difficult salt to work with due to its strongly hygroscopic behavior". This may also partly explain why previous data used to evaluate  $Q$  and  $W$  are discrepant. It is worth noting that good agreement between values reported by various authors (the first five rows in Table 3B) is not yet a guarantee of their accuracy.



*Empirical correlations for  $\Delta H_c$  and some remarks on  $\Delta H_c$  estimation*

Simple empirical or semi-empirical correlations proposed in refs. 4 and 18 for evaluating crystallization heats have also been tried for both salts studied. The differences between the values obtained from these correlations, eqns. (19), (20) and the values recommended above, are rather large: the relative differences are 9 and 45% for KCl and  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ , respectively, when eqn. (19) is used. The main advantage of eqn. (19) is that only  $\gamma_{\pm}(m_s)$  is required and not the full term  $W$  as in eqn. (7). However, in spite of an optimistic view by its author [4], it gives only a very rough estimate of  $\Delta H_c$ . Similarly eqn. (20) gives a value of  $\Delta H_c$  for KCl which differs by more than 20% from the above value of  $13.8 \text{ kJ mole}^{-1}$ . The constants in eqn. (20) are known for a few salts only and this equation has not been used in further works.

Since  $\text{dln } c/\text{d}(1/T) = \text{dln } m_s/\text{d}(1/T)$ , eqn. (21), proposed for estimation by Rychlý and Nývlt [7], can be rewritten as

$$\Delta H_c = -RQ$$

The terms  $W$  and  $P$  involved in the rigorous eqn. (7) are omitted. The more the terms  $W$  and  $P$  differ from unity, the greater differences are introduced in  $\Delta H_c$  by using this over-simplified relation. For anhydrous salts where  $P = 1$  and for ideal solutions where  $W = \nu$ , the inaccuracy of eqn. (21) stems only from omitting the factor  $\nu$ . For  $\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ , eqn. (21), as well as the corrected monograph given in refs. 7 and 9, yields  $\Delta H_c = 1.8 \text{ kJ mole}^{-1}$ , nearly one order of magnitude below the value recommended above. Similar unjustified application of an equation valid for an anhydrous salt, i.e. eqn. (7) where  $P = 1$ , to  $\text{LiCl} \cdot \text{H}_2\text{O}$  has been found in ref. 2. In order to check the reliability of the results for  $\Delta H_c$  calculated by Allakhverdov et al. [10] on the basis of the integral heats of dissolution taken from Parker's review [24], we have recalculated  $\Delta H_c$  from the same data using our extrapolation procedure described above. Since the published [10] and recalculated results differ considerably in some cases (see the comparison in Table 5), we prefer the value of  $\Delta H_c$  for KCl evaluated by us to that reported by Allakhverdov et al. [10].

TABLE 5  
Comparison of  $\Delta H_c$  values

|              | $\Delta H_c(\text{kJ mole}^{-1})$ |   |  |
|--------------|-----------------------------------|---|--|
|              | $\text{NaNO}_3$                   | $\text{NaI} \cdot 2 \text{H}_2\text{O}$ | $\text{NaBr} \cdot 2 \text{H}_2\text{O}$ |
| Ref. 10      | -11.46                            | -11.88                                  | -14.85                                   |
| Recalculated | $-13.0 \pm 0.6$                   | $-16.75 \pm 0.25$                       | $-16.6 \pm 0.1$                          |

## SYMBOLS

|                 |  |
|-----------------|--|
| $A, B, C$       | constants  |
| $\Delta H^0$    | heat of dissolution at infinite dilution                         |
| $\Delta H$      | integral heat of dissolution                                     |
| $K$             | constant = $1000/M_w = 55.50837$                                 |
| $\Delta L$      | differential heat of dissolution                                 |
| $M_1$           | molecular weight of solvent                                      |
| $M_w$           | molecular weight of water  |
| $P$             | stoichiometric term = $1 - n m_s/K$                              |
| $Q$             | temperature dependence of solubility, $d \ln m_s/dT^{-1}$        |
| $R$             | gas constant   |
| $T$             | temperature  |
| $W$             | term in eqn. (7) defined by eqn. (8)                             |
| $X, S$          | concentrations   |
| $a_i, b_i, c_i$ | constants  |
| $a_w$           | activity of water vapor  |
| $c$             | molar concentration  |
| $g(m)$          | arbitrary function of molal concentration                        |
| $m$             | molal concentration  |
| $m_s$           | molality at saturation   |
| $n$             | number of water molecules in one molecule of crystalhydrate salt |
| $\phi$          | molal osmotic coefficient  |
| $\phi_L$        | apparent molal heat content of solution                          |
| $\nu$           | number of ions in a molecule of salt                             |
| $\gamma_{\pm}$  | mean molal activity coefficient                                  |
| $\beta$         | constant   |

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