# ENTHALPY OF CRYSTALLIZATION OF POTASSIUM CHLORIDE FROM AQUEOUS SOLUTIONS AT TEMPERATURES BETWEEN 0 AND 100°C

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ABSTRACT

Enthalpies of crystallization of potassium chloride from aqueous solution were calculated using the description of thermodynamic properties recently derived by Holmes and Mesmer on the basis of the Pitzer model and Silvester and Pitzer correlations. Published experimental data were compared with those evaluated from the above model for the temperature range 0–100°C. Similar data for magnesium chloride hexahydrate are discussed.

INTRODUCTION

In contrast to the extensive literature on the properties of dilute aqueous solutions at room temperature, very little information is available on highly concentrated solutions at elevated temperatures. We did not find a satisfactory review on crystallization enthalpies of common inorganic salts from their aqueous solutions at higher temperatures. A single review was found on the crystallization enthalpies of sucrose over a wider temperature interval [1]. The aim of this paper is to estimate the enthalpy of crystallization for the $KCl–H_2O$ system over the temperature range 0–100°C, as a counterpart of our previous review on the present state of knowledge on the enthalpy of crystallization of this system at 25°C [2].

Practically no data have been found in the literature on the dilution or dissolution enthalpies of nearly saturated solutions of KCl at elevated temperatures, with the exceptions illustrated in Fig. 4 and discussed below. Therefore, our estimation was based on correlations of thermodynamic properties, which were derived for aqueous solutions of potassium chloride by Holmes and Mesmer [3] up to 250°C. This description is based on the Pitzer model of ion interaction [4], which was previously successfully used for a description of the $NaCl–H_2O$ system [5].

THEORETICAL

According to the resulting equations of Holmes and Mesmer [3], the temperature and concentration dependences of the relative apparent molal enthalpy of solution, $\phi_L$, and the molal osmotic coefficient, $\phi$, are given by *

$$\phi_L = \frac{2}{b} A_H \ln(1 + b\sqrt{m}) - 2RT^2(mB' + m^2C') \tag{1}$$

and

$$\phi = 1 - \frac{A_\phi\sqrt{m}}{1 + b\sqrt{m}} + mB_\phi + m^2C_\phi \tag{2}$$

where $B_\phi$ is defined by

$$B_\phi = \beta_0 + \beta_1 \exp(-\alpha\sqrt{m}) \tag{3}$$

$\alpha$ and $b$ are constants, which have been set at 2.0 and 1.2 $kg^{1/2}$ $mol^{-1/2}$, respectively, for all electrolytes where at least one of the ions is univalent. $\beta_0$, $\beta_1$ and $C_\phi$ are parameters of ionic interactions, which are specific for each individual electrolyte. These three parameters can all be described by arbitrary functions of temperature, g(T), of the form [3]

$$g(T) = p_1 + p_2\left(\frac{1}{T} - \frac{1}{T_r}\right) + p_3 \ln(T/T_r) + p_4(T - T_r) + p_5\left(T^2 - T_r^2\right)$$
$$+ p_6 \ln(T - 260) \tag{4}$$

where the reference temperature, $T_r$, is conveniently set at 298.15 K. The empirical constants, $p_i$, are summarized in Table 1, together with constants, $q_i$, of temperature dependence of an integral enthalpy of dissolution at infinite dilution, $\Delta H^0$

$$\Delta H^0(T) = q_1 + q_2T + q_3T^2 + q_4T^3 + q_5 \ln(T - 270) \tag{5}$$

and of the heat capacity of the pure solid, KCl, $c_{p_2^0(s)}$

$$c_{p_2^0(s)} = q_6 + q_7T \tag{6}$$

All equations of the Pitzer model given here are specific for univalent electrolytes; for general equations see ref. 5. $A_H$ and $A_\phi$ are Debye–Hückel limiting law parameters for enthalpy and osmotic coefficient, respectively, and their values, which were evaluated by Silvester and Pitzer [5], are shown in Table 2 together with $A_J$, the Debye–Hückel heat capacity parameter.

Parameters $C'$ and $B'$ in eqn. (1) represent temperature derivations

$$B' = (\partial B/\partial T)_{m,P} \text{ and } C' = (\partial C_\phi/\partial T)_{m,P}/2$$

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* The notation in most cases is the same as used in ref. 3.

TABLE 1

Parameters of temperature dependence of the ion interaction model for the KCl–H$_2$O system

| $i$ | function | $p_{1,i}$ | $p_{2,i}$ | $p_{3,i}$ | $p_{4,i}$ | $p_{5,i}$ | $p_{6,i}$ |
|---|---|---|---|---|---|---|---|
| 1 | $\beta_0$ (kg mol$^{-1}$) | 0.04808 | −758.48 | −4.7062 | 0.010072 | $-3.7599 \times 10^{-6}$ | – |
| 2 | $\beta_1$ (kg mol$^{-1}$) | 0.0476 | 303.9 | 1.066 | – | – | 0.047 |
| 3 | $C_\phi$ (kg$^2$ mol$^{-2}$) | $-7.88 \times 10^{-4}$ | 91.27 | 0.58643 | $-1.298 \times 10^{-3}$ | $4.9567 \times 10^{-7}$ | – |

| | $q_1$ | $q_2$ | $q_3$ | $q_4$ | $q_5$ |
|---|---|---|---|---|---|
| $\Delta H^0$ (kJ mol$^{-1}$) | $1.5774 \times 10^5$ | −1037.86 | 2.7739 | −0.00284332 | −686 |

| | $q_6$ | $q_7$ |
|---|---|---|
| $c_{p_2}^0$(s) (J mol$^{-1}$ K$^{-1}$) | 46.35 | 0.01672 |

TABLE 2

Debye–Hückel parameters for the osmotic coefficients, enthalpy and heat capacity

| $t$ (°C) | $A_\phi$ ($kg^{-1/2}$ $mol^{-1/2}$) | $A_H$ ($J$ $mol^{-1}$) | $A_J$ ($J$ $mol^{-1}$ $K^{-1}$) |
|---|---|---|---|
| 0 | 0.3770 | 1719.6 | 40.17 |
| 10 | 0.3820 | 2158.9 | 47.28 |
| 20 | 0.3878 | 2656.8 | 51.46 |
| 25 | 0.3910 | 2920.4 | 53.56 |
| 30 | 0.3944 | 3188.2 | 55.29 |
| 40 | 0.4017 | 3761.4 | 59.41 |
| 50 | 0.4098 | 4376.5 | 63.60 |
| 60 | 0.4185 | 5033.4 | 68.20 |
| 70 | 0.4279 | 5740.5 | 73.64 |
| 80 | 0.4380 | 6506.1 | 79.50 |
| 90 | 0.4488 | 7334.6 | 86.61 |
| 100 | 0.4603 | 8238.3 | 94.14 |

These values were taken from Table II of ref. 5, and were recalculated by using 1 cal = 4.184 J. In fact, values of $A_H/3$ and $A_J/3$ were substituted into the equations instead of $A_H$ and $A_J$, since the Holmes–Mesmer [3] equations differ from those given by Silvester and Pitzer [5] just by these factors. We prefer to keep the form of equations and values of parameters $A_J$, $A_H$ given in the original works [3,5].

where

$$B = \beta_0 + 2\beta_1 P(m) \tag{7}$$

and

$$P(m) = \left[1 - (1 + \alpha\sqrt{m})\exp(-\alpha\sqrt{m})\right]/(\alpha^2 m) \tag{8}$$

The enthalpy of crystallization, $\Delta H_C$, may be evaluated from the relation (valid for anhydrous salts)

$$-\Delta H_C = \Delta H^0(T) + \overline{L}_2(m_s, T)$$
$$= \Delta H^0(T) + \phi_L(m_s, T) + m_s d\phi_L(T)/dm \,|_{m_s} \tag{9}$$

or from an equivalent form

$$-\Delta H_C = \Delta H^0(T) + \phi_L(m_s, T) + (\sqrt{m}/2)d\phi_L(T)/d\sqrt{m} \,|_{m_s} \tag{10}$$

Alternatively, the enthalpy of crystallization follows from the temperature dependence of solubility

$$Q = -d \ln m_s/d(1/T) \tag{11}$$

and from the osmotic coefficient data term

$$W = \nu\left[\phi + (d\phi/d \ln m)_{T,P}\right]_{m_s} \tag{12}$$

Equivalent expressions for the term $W$, by using activity coefficients, activity of water or vapour pressure of water over the solutions, or the van't Hoff

deviation function, were derived by Williamson [6]. The form of eqn. (12) was preferred here only due to a lower sensitivity to a numerical error in the concentration slope of these colligative properties.

For anhydrous salts [6]

$$-\Delta H_C = RQW \tag{13}$$

where $R$ is the universal gas constant, set at 8.3144 J K$^{-1}$ mol$^{-1}$. Molality at saturation, $m_s$, was calculated from the empirical equations given by Broul et al. [7] for $T \in (273\text{--}373)$ K by

$$m_s = (1000/M_W) X/(1 - X)$$

where the molar fraction $X$ is given by

$$\log_{10} X = A + B/T + C \log_{10} T \tag{14}$$

This correlation with $A = 6.75911$, $B = -604.3346$ and $C = -2.357052$ fits the set of experimental data summarized by Linke and Seidell [8]. The term $Q$ is thus given by

$$Q = (B \ln 10 - CT)/(1 - X) \tag{15}$$

Slightly lower values of $m_s$ and $Q$ follow from the new correlation of solubility, $S$ (wt%) by Potter and Clynne [9]

$$S = 22.055 + 0.1793t - 4.373 \times 10^{-4} t^2 \tag{16}$$

where $t$ is the temperature in degrees Celsius, so that

$$Q = T^2 \, 100(0.1793 - 8.746 \times 10^{-4} t)/S(100 - S) \tag{17}$$

where $T = 273.15 + t$ and $m_s = 1000S/[(100 - S)M_2]$, where $M_2 = 74.551$ for KCl.

It is convenient to denote the function g$(T)$ for $\beta_0$, $\beta_1$ and $C_\phi$ as $g_1$, $g_2$ and $g_3$, respectively. Their temperature derivations are denoted as $g_4$, $g_5$ and $g_6$

$$g_{i+3} = (\partial g_i/\partial T)_{m,P} \qquad \text{for } i = 1, 2, 3 \tag{18}$$

and, similarly, the second derivatives are $g_7$, $g_8$ and $g_9$, respectively, where

$$g_{i+3} = (\partial g_i/\partial T)_{m,P} \qquad \text{for } i = 4, 5, 6$$

Of course, for $i = 4, 5, 6$

$$g_i = p_{4,i} + 2p_{5,i}T + p_{3,i}/T + p_{6,i}/(T - 260) - p_{2,i}/T^2 \tag{19}$$

and for $i = 7, 8, 9$

$$g_i = 2(p_{5,i} + p_{2,i}/T^3) - p_{3,i}/T^2 - p_{6,i}/(T - 260)^2 \tag{20}$$

To complete the set of working equations it is useful to write

$$m(d\phi_L/dm)_{T,P} = A_H \frac{\sqrt{m}}{1 + 1.2\sqrt{m}} - 2RT^2 m[g_4 + \exp(-\alpha\sqrt{m})g_5 + mg_6] \tag{21}$$
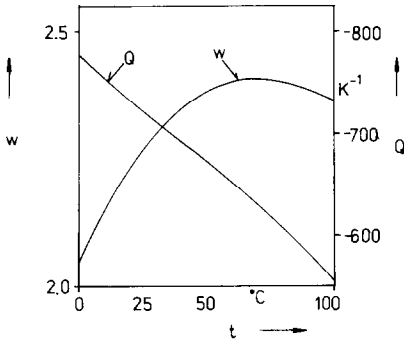
Fig. 1. Temperature dependences of terms $Q$ and $W$ evaluated by using solubilities of Potter and Clynne [9] (eqn. 16), evaluated from eqns. (12), (23) and (24).

and

$$\phi_L = \frac{2}{b} A_H \ln(1 + b\sqrt{m}) - 2RT^2 m(g_4 + 2g_5 P + mg_6/2) \qquad (22)$$

The enthalpy of crystallization may be evaluated from these equations by using solubility correlations (14) and/or (16), and eqns. (5), (9), (19), (21) and (22). The second alternative is based on eqn. (13), with eqns. (15) or (17) and the term $W$, which is given by eqns. (12), (23) and (24)

$$\phi(m_s) = 1 - A_\phi \frac{\sqrt{m_s}}{1 + b\sqrt{m_s}} + m_s\left[g_1 + g_2 \exp\left(-\alpha\sqrt{m_s}\right)\right] + m_s^2 g_3 \qquad (23)$$

$$\left(\frac{d\phi}{d \ln m}\right)_{T,P}\bigg|_{m_s} = -A_\phi \frac{\sqrt{m_s}}{2\left(1 + b\sqrt{m_s}\right)^2} + m_s\left[g_1 + \left(1 - \sqrt{m_s}\right)\exp\left(-\alpha\sqrt{m_s}\right)g_2\right]$$
$$+ 2m_s^2 g_3 \qquad (24)$$

The temperature dependence of the terms $Q$ and $W$, as evaluated from
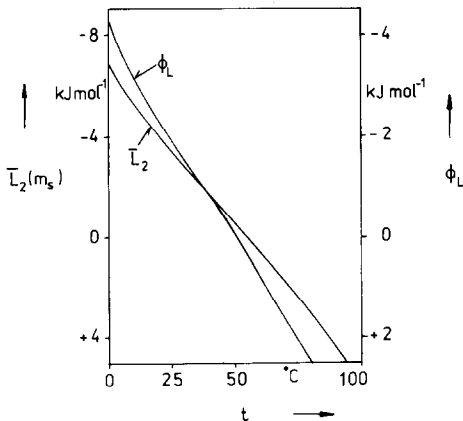


Fig. 2. Temperature dependence of apparent relative molal enthalpy of solution at saturation, $\phi_L(m_s)$, and partial molal enthalpy of KCl at saturated solution, $\bar{L}_2(m_s)$, evaluated from eqns. (22) and (21).
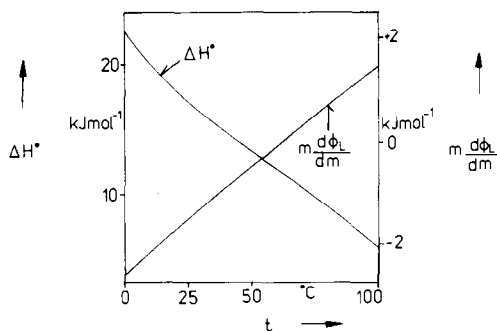
Fig. 3. Temperature dependence of dissolution enthalpy of KCl at infinite dilution, $\Delta H^0$, evaluated according to eqn. (5) and concentration slope of the dependence of $\phi_L(m)$ (evaluated from eqn. 21), which is proportional to the partial molal enthalpy of water at saturated solution

$$\bar{L}_1(m_s) = - \frac{M_1}{1000} m_s \left( \frac{d\phi_L}{d \ln m_s} \right)_{P,T|m_s}$$

solubilities given by eqns. (16)–(18), are illustrated in Fig. 1. From their mutually opposite courses and the non-monotonous character of the function $W(t)$, the course of the resulting function $\Delta H_C(t)$ follows. The individual terms for computing the enthalpy of crystallization from the first alternative, i.e., from eqns. (9)–(11), are shown in Figs. 2 and 3. The resulting enthalpy of crystallization, evaluated from both correlations of solubilities, are summarised in Table 3C and are depicted in Fig. 4, where

TABLE 3

Calculated values of enthalpies of crystallization for various temperatures and of related thermodynamic characteristics

TABLE 3A

| $t$ (°C) | $m_s$ [a] (mol kg$^{-1}$) | $m_s$ [b] (mol kg$^{-1}$) | $-Q$ [a] (K) | $-Q$ [b] (K) | $W$ [a] | $W$ [b] |
|---|---|---|---|---|---|---|
| 0 | 3.775 | 3.795 | 798.55 | 778.20 | 2.044 | 2.048 |
| 10 | 4.180 | 4.191 | 779.66 | 753.89 | 2.148 | 2.149 |
| 20 | 4.586 | 4.583 | 758.4 | 732.60 | 2.234 | 2.234 |
| 25 | 4.787 | 4.778 | 748.2 | 722.7 | 2.270 | 2.269 |
| 30 | 4.988 | 4.971 | 737.8 | 713.0 | 2.303 | 2.300 |
| 40 | 5.386 | 5.354 | 716.8 | 694.1 | 2.354 | 2.350 |
| 50 | 5.775 | 5.729 | 695.4 | 675.1 | 2.388 | 2.384 |
| 60 | 6.154 | 6.094 | 673.5 | 655.5 | 2.407 | 2.403 |
| 70 | 6.521 | 6.448 | 651.2 | 634.2 | 2.412 | 2.409 |
| 80 | 6.875 | 6.778 | 628.4 | 611.2 | 2.405 | 2.402 |
| 90 | 7.214 | 7.112 | 605.2 | 585.8 | 2.386 | 2.386 |
| 100 | 7.536 | 7.419 | 581.5 | 557.7 | 2.359 | 2.360 |

TABLE 3B

| $t$ (°C) | $\phi(m_s)$ (kJ mol⁻¹) | $\left.\dfrac{d\phi}{d\ln m}\right|_{m_s}$ (kJ mol⁻¹) | $\phi_L(m_s)$ (kJ mol⁻¹) | $\left.\dfrac{d\phi_L}{d\ln m}\right|_{m_s}$ (kJ mol⁻¹) | $\bar{L}_2(m_s)$ (kJ mol⁻¹) | $\bar{L}_1(m_s)$ (kJ mol⁻¹) |
|---|---|---|---|---|---|---|
| 0 | 0.9221 | 0.1017 | −4.319 | −2.6341 | −6.953 | 0.1805 |
| 10 | 0.9517 | 0.1228 | −3.116 | −2.150 | −5.266 | 0.163 |
| 20 | 0.9775 | 0.1392 | −2.281 | −1.724 | −4.006 | 0.143 |
| 25 | 0.9890 | 0.1455 | −1.898 | −1.516 | −3.414 | 0.131 |
| 30 | 0.9996 | 0.1506 | −1.524 | −1.309 | −2.834 | 0.117 |
| 40 | 1.0181 | 0.1572 | −0.768 | −0.896 | −1.665 | 0.087 |
| 50 | 1.0329 | 0.1592 | 0.008 | −0.487 | −0.479 | 0.050 |
| 60 | 1.0443 | 0.1573 | 0.812 | −0.085 | 0.727 | 0.001 |
| 70 | 1.0525 | 0.1519 | 1.651 | 0.311 | 1.962 | −0.036 |
| 80 | 1.0576 | 0.1436 | 2.533 | 0.700 | 3.233 | −0.086 |
| 90 | 1.0599 | 0.1329 | 3.460 | 1.083 | 4.543 | −0.139 |
| 100 | 1.0596 | 0.1205 | 4.443 | 1.463 | 5.906 | −0.196 |

TABLE 3C

| $t$ (°C) | $\Delta H^0$ (kJ mol⁻¹) | $-\Delta H_C$ [a] (kJ mol⁻¹) | $-\Delta H_C$ [b] (kJ mol⁻¹) | $-\Delta H_C$ [c] (kJ mol⁻¹) | $-\Delta H_C$ [d] (kJ mol⁻¹) |
|---|---|---|---|---|---|
| 0 | 22.478 | 15.542 | 15.525 | 13.573 | 13.248 |
| 10 | 19.950 | 14.690 | 14.684 | 13.903 | 13.471 |
| 20 | 18.086 | 14.080 | 14.081 | 14.086 | 13.604 |
| 25 | 17.236 | 13.820 | 13.822 | 14.123 | 13.633 |
| 30 | 16.418 | 13.583 | 13.585 | 14.125 | 13.637 |
| 40 | 14.854 | 13.189 | 13.190 | 14.029 | 13.564 |
| 50 | 13.348 | 12.874 | 12.869 | 13.808 | 13.382 |
| 60 | 11.871 | 12.609 | 12.597 | 13.480 | 13.093 |
| 70 | 10.397 | 12.379 | 12.359 | 13.060 | 12.700 |
| 80 | 8.905 | 12.167 | 12.138 | 12.564 | 12.207 |
| 90 | 7.376 | 11.958 | 11.919 | 12.007 | 11.619 |
| 100 | 5.790 | 11.746 | 11.696 | 11.406 | 10.943 |

Values of enthalpy of crystallization were calculated from:
[a] eqn. (9), considering solubilities eqn. (14), curve (a) in Fig. 4;
[b] eqn. (9), considering solubilities eqn. (16), curve (b) in Fig. 4;
[b] eqn. (13), considering solubilities eqn. (14), curve (c) in Fig. 4;
[d] eqn. (13), considering solubilities eqn. (16), curve (d) in Fig. 4.

the experimental data given by various authors are also included. The temperature derivative of the integral heat of dissolution is given by [11]

$$\frac{d\Delta H_m}{dT} = \phi_{c_p} - c_{p_2^0(s)} \tag{25}$$

For the apparent molal heat capacity, $\phi_{c_p}$, the following holds [3]

$$\phi_{c_p} = c_{p_2^0(s)} + \left(\partial \Delta H^0(T)/\partial T\right)_P + \left(\partial \phi_L/\partial T\right)_{P,m} \tag{26}$$
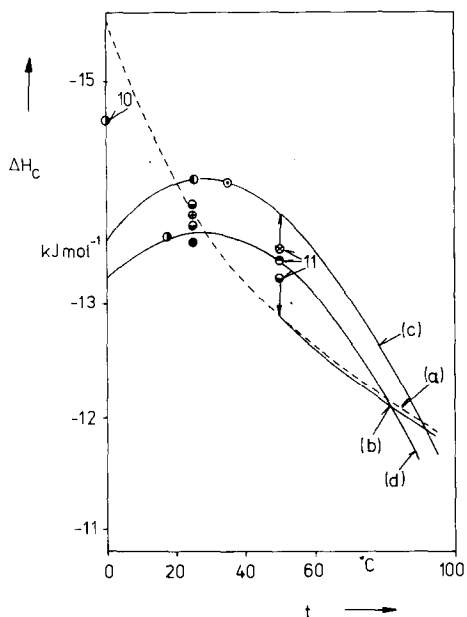
Fig. 4. Temperature dependence of enthalpy of crystallization following from Holmes and Mesmer [3] correlations by using two alternatives of the basic equation (eqns. 9 and 13), each for two standard empirical correlations of solubility, given by eqns. (14) and (16), see Table 3C. Literature data are denoted as follows: (◐) Mondain Monval (cited according to ref. 10); (◑) evaluated from Table 1 of ref. 11; (◕) evaluated from Table 4 of ref. 11; (⊗) evaluated from Fig. 4 of ref. 11; (○) value given by Glasner and Kenat [17]; (⊕) value recommended in ref. 5, which is based on results given in refs. 6, 12, 14, 15 and 16; (●) ref. 13.

| Curve | a | b | c | d |
|---|---|---|---|---|
| (eqn.) | (9) | (9) | (13) | (13) |
| $m_s$ (eqn.) | (14) | (16) | (16) | (14) |

Considering eqns. (25), (26), (5), (6) and (22), it follows that

$$\frac{d\Delta H_m}{dT} = \frac{A_J}{b}\ln(1 + b\sqrt{m}) - 2RT\left[m(2B' + TB'') + m^2(2C' + TC'')\right] + q_2$$

$$+ 2q_3T + 3q_4T^2 + q_5/(T - 270) \tag{27}$$

where

$$B'' = \partial B'/\partial T = g_7 + 2g_8P(m) \tag{28}$$

$$C'' = \partial C'/\partial T = g_9/2 \tag{29}$$

For several temperature levels the temperature derivative, $d\Delta H_m/dT$, according to eqn. (27) is shown in Fig. 5. For the final evaluation of the
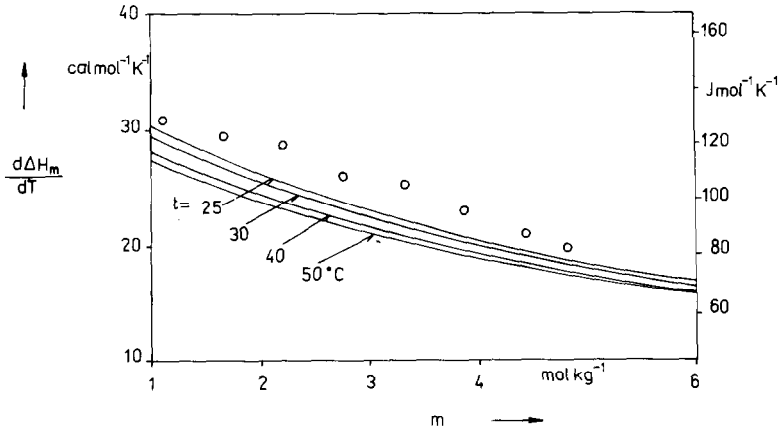
Fig. 5. Concentration dependence of temperature coefficient of integral enthalpy of dissolution evaluated from model eqn. (25). (○) data of the coefficient for the temperature range 25–50°C given by Kaganovich and Mishschenko [11].

temperature dependence of enthalpy of crystallization, $d\Delta H_C/dT$, since

$$\Delta H_C = -\left[\Delta H_m + m\frac{d\Delta H_m}{dm}\right]_{m_s} = -\left[\Delta H_m - \frac{1000}{M_1 m_s}\overline{L}_1\right]_{m_s} \tag{30}$$

then

$$-\frac{d\Delta H_C}{dT} = \frac{d\Delta H_m}{dT} - \frac{1000}{M_1}\frac{1}{m_s}\frac{d\overline{L}_1(m_s)}{dT} \tag{31}$$

Further, from, e.g., Mishschenko and Poltoratskii [18]

$$\frac{d\overline{L}_1}{dT} = -\frac{mM_1}{1000}\frac{\sqrt{m}}{2}\frac{d\phi_{c_p}}{d\sqrt{m}} \tag{32}$$

and the term $d\Delta H_m/dT$ is given by eqn. (27), we have

$$-\frac{d\Delta H_C}{dT} = \frac{d\Delta H_m}{dT} + \frac{\sqrt{m_s}}{2}\frac{d\phi_{c_p}}{d\sqrt{m}}\bigg|_{m_s} \tag{33}$$

where

$$\frac{\sqrt{m_s}}{2}\frac{d\phi_{c_p}}{d\sqrt{m}}\bigg|_{m_s} = \frac{A_J}{2}\frac{\sqrt{m_s}}{\left(1 + b\sqrt{m_s}\right)} - 2m_s RT\big\{2B' + TB''$$

$$+ \left[\exp\left(-\alpha\sqrt{m_s}\right) - 2P(m_s)\right](2g_5 + Tg_8)$$

$$+ 2m_s(g_6 + Tg_9/2)\big\} \tag{34}$$

The temperature coefficient, $d\Delta H_C/dT$, as a function of temperature evaluated from the above equations is plotted in Fig. 6, where the coeffi-
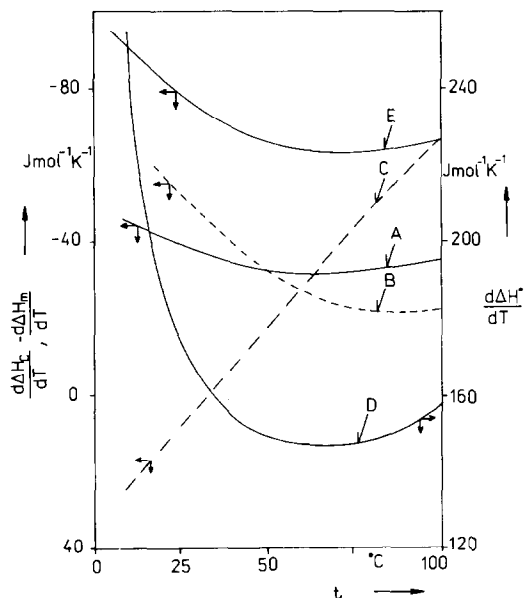
Fig. 6. Comparison of temperature coefficients $d\Delta H^0/dT$, $d\Delta H_m/dT$ and $d\Delta H_C/dT$ evaluated from model Holmes and Mesmer [3]. $d\Delta H_C/dT$ curve A given by eqn. (33); $d\Delta H_C/dT$ curve B from Fig. 4 curve (b); $d\Delta H_C/dT$ curve C from Fig. 4 curve (d); $d\Delta H^0/dT$ curve D from eqn. (5); $d\Delta H_m/dT$ curve E from eqn. (25).
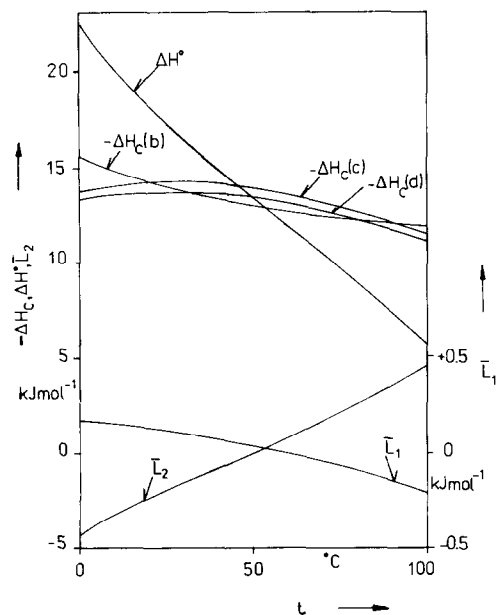


Fig. 7. Survey of temperature dependences of the thermodynamics characteristics $\Delta H^0$, $\Delta H_C$, $\bar{L}_2(m_s)$ and $\bar{L}_1(m_s)$ of aqueous solutions of KCl.

cients $d\Delta H^{0}/dT$ and $d\Delta H_{m}(m_{s})/dT$ are also included. An overall view on the resulting characteristic enthalpies is given in Fig. 7.

DISCUSSION

From the temperature dependences of all thermodynamic quantities shown in Fig. 7 and in Figs. 1–3, it is clear that the enthalpy of crystallization depends only very weakly on temperature. Mutual relationships between all three temperature coefficients, $d\Delta H^{0}/dT$, $d\Delta H_{m}(m_{s})/dT$ and $d\Delta H_{C}/dT$, and their dependences on concentration and temperature obey the main rules given by Mishschenko (see, e.g., refs. 11, 18, 19). Usually, $d\Delta H^{0}/dT$ and $d\Delta H_{m}/dT$ are negative, i.e., with increasing temperature the dissolution process becomes less endothermic, and/or becomes more exothermic: the enthalpy of dissolution represents the difference between the lattice enthalpy of a crystal, $\Delta H_{L}$, and the enthalpy of hydration of ions, $\Delta H_{h}$, the endothermic effect of destroying this crystal lattice depends only weakly on temperature, the resulting dependence of enthalpy of dissolution on $T$ is more or less given by the temperature dependence of the enthalpy of hydration. With increasing concentration and temperature, the absolute values of these coefficients decrease (i.e., coefficients become less negative). In other words, with increasing temperature and concentration the role of effects independent of temperature becomes more and more important. These qualitative features are partly illustrated in Table 3B and C.

For the KCl–H$_2$O system the decrease in $d\Delta H_{m}/dT$ with increasing concentration is given in Fig. 5. The experimental data given by Kaganovich and Mishschenko [11] are about a few per cent higher than are those evaluated from the Holmes and Mesmer equations [3], but their trends agree well. Further, the temperature coefficients derived from the Holmes and Mesmer model [3] shown in Fig. 6, decrease with increasing temperature with the exception of curve C; this curve represents the coefficient $d\Delta H_{C}/dT$ evaluated from eqn. (13). It is clear on comparison of the resulting enthalpy of crystallization vs. temperature plots in Fig. 4, that $\Delta H_{C}$ values evaluated from solubilities and osmotic coefficients (i.e., from eqn. 13), differ considerably in $d\Delta H_{C}/dT$ from those following from the enthalpy of dissolution (i.e., from eqns. 9 or 10). This means that at saturation concentration, the set of equations given by Holmes and Mesmer [3] is not entirely internally consistent, at least near zero Celsius temperature, where the above difference reaches its maximum. This is partly a consequence of the fact that in deriving their best-fit parameters, Holmes and Mesmer [3] excluded some data for highly concentrated solutions, and other data for high concentrations were taken with low weights. Considering the above rules according to Mishschenko [11,18,19], one could prefer the more simple, monotonous curves (a) or (b) in Fig. 4, prior to curves (c) and (d).

However, the non-monotonous temperature dependence of osmotic and activity coefficients for KCl [22] as well as for NaCl [23] is well known. The dependence of the osmotic term, $W$, on temperature, which is given in Fig. 1, is also not monotonous. Together with the simple dependence of the solubility slope, $Q$, on temperature, the resulting enthalpy of crystallization, $\Delta H_C$, following from eqn. (13), is based on a sufficient experimental basis and should not be neglected. The discrepancy of the enthalpy of crystallization following from the two alternatives may be resolved when a reliable enthalpy of dissolution is known at low (near zero Celsius temperature) and at high (above $t = 60°C$) temperatures up to saturation.

In a paper given by Kaganovich and Mishschenko [11] there are three different concentration dependences of an integral enthalpy of dissolution of KCl in water at 50°C. Therefore, three different values of $\Delta H_C$, following from the data in Tables 1 and 4, and Fig. 6 of their work [11], are shown in Fig. 4 together with an uncertainty interval of the value evaluated from their Table 1. It seems likely that their data [11] of the coefficients $d\Delta H_m/dT$, which are given in Fig. 5, are similarly uncertain. It is possible that this uncertainty may be higher than the difference between their values (average values for the range 25–50°C) and the curves representing the Holmes and Mesmer model [1].

*MgCl₂–H₂O system*

In a previous study [2] this system was dealt with as an example for which very limited data are available in contrast to the KCl–H₂O system.

For the $MgCl_2 \cdot 6H_2O–H_2O$ system the enthalpy of crystallization from dissolution enthalpies and that from solubility and osmotic data were discrepant even at 25°C [2].Mishschenko and Yakolev [19] measured dilution enthalpies of solutions of $MgCl_2 \cdot 6H_2O$ of different concentrations at $+2$ and $-6°C$, and were able to evaluate a concentration dependence of the integral enthalpy of dissolution for these temperatures. By using relationships between $\Delta H^0$, $\overline{L}_2$, $\overline{L}_1$ and enthalpy of crystallization

$$-(\Delta H_C)_{MgCl_2} = (\Delta H^0)_{MgCl_2} + \overline{L}_2(m_s) \tag{35}$$

$$-(\Delta H_C)_{MgCl_2 \cdot 6H_2O} = (\Delta H^0)_{MgCl_2 \cdot 6H_2O} + \overline{L}_2(m_s) + 6\overline{L}_1(m_s) \tag{36}$$

it is possible to evaluate the enthalpy of crystallization of hexahydrate for both temperatures and for anhydrous salt at 25°C (see Table 4). We have not found $\Delta H^0$ values of anhydrous $MgCl_2$ at $+2°C$, from which the desired value of $\Delta H_C$ may be evaluated from eqn. (35). The value of $\Delta H^0$ for the anhydrous salt at 25°C was taken from ref. 20. Since the value of $\Delta H_C$ for $MgCl_2 \cdot 6H_2O$ at 25°C independently measured by the above author [19] agrees well with previous data following from dissolution enthalpies [2], it remains open to doubt whether the higher value of $\Delta H_C$ ($-15.8$ kJ mol$^{-1}$),

TABLE 4

Comparison of enthalpy of dissolution at infinite dilution and of enthalpy of crystallization for $MgCl_2 \cdot 6H_2O$ and $MgCl_2$ (values were evaluated from data given in refs. 18 and 19)

| Salt | $t$ (°C) | $m_s$ (mol kg$^{-1}$) | $\Delta H^0$ (kJ mol$^{-1}$) | $\bar{L}_2(m_s)$ (kJ mol$^{-1}$) | $\bar{L}_1(m_s)$ (kJ mol$^{-1}$) | $\Delta H_C$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|
| $MgCl_2$ | 25 | 5.80 | $-154.9$ | 41.42 | $-2.18$ | 113.5 |
| $MgCl_2 \cdot 6H_2O$ | 25 | 5.80 | $-16.02$ | 41.42 | $-2.18$ | $-12.34$ |
| $MgCl_2 \cdot 6H_2O$ | 2 | 5.59 | $-10.46$ | 39.25 | $-1.97$ | $-16.99$ |

following from recent data on osmotic coefficients and solubility, should be accepted as previously recommended [2].

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