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Estimation of the heat of fusion of binary compounds and of eutectic using thermodynamic balances

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Abstract

Relations to calculate estimated enthalpies of fusion of binary compounds and eutectics at their equilibrium temperature in binary systems of inorganic substances, based on entropy or enthalpy balances, are presented. Their simplified forms were applied to estimate the enthalpy of fusion of equimolar compounds and binary eutectics in the Na_2SO_4–NaF and K_2SO_4–KF systems. Estimated enthalpies of fusion of $NaF \cdot Na_2SO_4$ and $KF \cdot K_2SO_4$ depend on simplified assumptions used for the calculation and are 7–13% lower than measured values. Relative errors of estimated enthalpies of fusion for eutectics, related to the values of these quantities calculated using experimental heats of fusion of binary compounds and measured enthalpies of mixing at corresponding eutectic composition, are within the limits 0–12% depending on input quantities.

INTRODUCTION

For numerical thermodynamic analyses of the phase diagrams of A–B systems whose components form a binary, partially or totally dissociated, compound, it is necessary to know as input quantities, the enthalpies of fusion of this compound, of the components and of both eutectics. If there is a deficiency in the available data, their estimations can be used.

The aim of this paper is to determine the estimations for the enthalpies of fusion of binary compounds and eutectics in binary systems of inorganic substances, using entropy or enthalpy balances.

THEORETICAL

The enthalpy of fusion of binary compounds A_qB_r in the A–B system calculated on the basis of the entropy balance

The entropy of the melt A_qB_r at its temperature of fusion $S_{melt}(A_qB_r, T_{fus}(A_qB_r))$ can be determined in two ways

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(a) By adding the entropy of the crystalline substance A_qB_r at its temperature of fusion $S_{cr}(A_qB_r, T_{fus}(A_qB_r))$ and the entropy of fusion at this temperature $\Delta S_{fus}(A_qB_r, T_{fus}(A_qB_r))$

$$S_{melt}(A_qB_r, T_{fus}(A_qB_r)) = S_{cr}(A_qB_r, T_{fus}(A_qB_r)) + \Delta S_{fus}(A_qB_r, T_{fus}(A_qB_r)) \quad (1)$$

(b) By adding the entropy of the mechanical mixture of melts of A and B in the corresponding stoichiometric ratio at the temperature of fusion $T_{fus}(A_qB_r)$ and the entropy of mixing of this mixture at the same temperature $\Delta S_{mix,melt}(A_qB_r, T_{fus}(A_qB_r))$

$$\begin{aligned} S_{melt}(A_qB_r, T_{fus}(A_qB_r)) = {} & qS_{melt}(A, T_{fus}(A_qB_r)) \\ & + rS_{melt}(B, T_{fus}(A_qB_r)) \\ & + \Delta S_{mix,melt}(A_qB_r, T_{fus}(A_qB_r)) \end{aligned} \quad (2)$$

We substitute into eqn. (2) from the relation

$$\begin{aligned} \Delta S_{mix,melt}(A_qB_r, T_{fus}(A_qB_r)) = {} & \frac{\Delta H_{mix,melt}(A_qB_r, T_{fus}(A_qB_r))}{T_{fus}(A_qB_r)} \\ & - R[q \ln a(A, \text{melt}, T_{fus}(A_qB_r)) \\ & + r \ln a(B, \text{melt}, T_{fus}(A_qB_r))] \end{aligned} \quad (3)$$

where

$$a(X) = \gamma(X)x(X) \quad (3a)$$

In eqn. (3a), $a(X)$, $\gamma(X)$ and $x(X)$ are the activity, activity coefficient and mole fraction of X ($X \equiv A$ or B, $x(A) = q/(q+r)$, $x(B) = r/(q+r)$), respectively.

From equal values of $S_{melt}(A_qB_r, T_{fus}(A_qB_r))$ determined according to eqns. (1) and (2), the unknown value of $\Delta H_{fus}(A_qB_r, T_{fus}(A_qB_r))$ can be calculated from eqn. (4)

$$\begin{aligned} & \Delta H_{fus}(A_qB_r, T_{fus}(A_qB_r)) \\ & = T_{fus}(A_qB_r)\Bigg\{q\Bigg[\int_0^{T_{fus}(A)} \frac{C_{p,cr}(A, T)}{T} dT + \Delta S_{fus}(A, T_{fus}(A)) \\ & \quad + \int_{T_{fus}(A)}^{T_{fus}(A_qB_r)} \frac{C_{p,melt}(A, T)}{T} dT\Bigg] \\ & \quad + r\Bigg[\int_0^{T_{fus}(B)} \frac{C_{p,cr}(B, T)}{T} dT + \Delta S_{fus}(B, T_{fus}(B)) + \int_{T_{fus}(B)}^{T_{fus}(A_qB_r)} \frac{C_{p,melt}(B, T)}{T} dT\Bigg] \\ & \quad + \frac{\Delta H_{mix,melt}(A_qB_r, T_{fus}(A_qB_r))}{T_{fus}(A_qB_r)} \\ & \quad - R[q \ln a(A, \text{melt}, T_{fus}(A_qB_r)) + r \ln a(B, \text{melt}, T_{fus}(A_qB_r))] \\ & \quad - \int_0^{T_{fus}(A_qB_r)} \frac{C_{p,cr}(A_qB_r, T)}{T} dT\Bigg\} \end{aligned} \quad (4)$$

It is assumed in eqn. (4) that the temperature dependences of the heat capacities of the crystalline substances are known over the temperature range from absolute zero to the temperature of fusion.

If the heat capacity of the crystalline compound A_qB_r is not known, it can be substituted as a first approximation, according to Neumann–Kopp's law, by the addition of the heat capacities of the crystalline components multiplied by the corresponding stoichiometric coefficient

$$C_{p,\mathrm{cr}}(A_qB_r, T) = qC_{p,\mathrm{cr}}(A, T) + rC_{p,\mathrm{cr}}(B, T) \tag{5}$$

Substituting eqn. (5) into eqn. (4) and using the relation

$$\Delta C_{p,\mathrm{fus}}(X, T) = C_{p,\mathrm{melt}}(X, T) - C_{p,\mathrm{cr}}(X, T) \tag{6}$$

eqn. (4) is simplified to the form

$$\begin{aligned}
&\Delta H_{\mathrm{fus}}(A_qB_r, T_{\mathrm{fus}}(A_qB_r)) \\
&\quad = T_{\mathrm{fus}}(A_qB_r)\Bigg\{q\left[\Delta S_{\mathrm{fus}}(A, T_{\mathrm{fus}}(A)) + \int_{T_{\mathrm{fus}}(A)}^{T_{\mathrm{fus}}(A_qB_r)} \frac{\Delta C_{p,\mathrm{fus}}(A, T)}{T}\,\mathrm{d}T\right] \\
&\qquad + r\left[\Delta S_{\mathrm{fus}}(B, T_{\mathrm{fus}}(B)) + \int_{T_{\mathrm{fus}}(B)}^{T_{\mathrm{fus}}(A_qB_r)} \frac{\Delta C_{p,\mathrm{fus}}(B, T)}{T}\,\mathrm{d}T\right] \\
&\qquad + \frac{\Delta H_{\mathrm{mix,melt}}(A_qB_r, T_{\mathrm{fus}}(A_qB_r))}{T_{\mathrm{fus}}(A_qB_r)} \\
&\qquad - R[q \ln a(A, \mathrm{melt}, T_{\mathrm{fus}}(A_qB_r)) + r \ln a(B, \mathrm{melt}, T_{\mathrm{fus}}(A_qB_r))]\Bigg\}
\end{aligned} \tag{7}$$

The values for the enthalpy of mixing are for 1 mole of mixture $(A_{q/(q+r)}B_{r/(q+r)})$ in the binary system A–B. To recalculate the value for the enthalpy of mixing of the mixture at the composition corresponding to A_qB_r, this value has to be multiplied by the sum of the stoichiometric coefficients, $(q + r)$. The activities or activity coefficients of the constituents in the melt are functions of the equilibrium degree of dissociation α according to the scheme

$$A_qB_r \rightarrow qA + rB \tag{A}$$

At equilibrium, the constituents A, B and A_qB_r are present in the melt in the ratio $\alpha q : \alpha r : (1 - \alpha)$.

The enthalpy of fusion of binary eutectics in the A–B system determined on the basis of the enthalpy or entropy balance

The enthalpy of fusion for a eutectic can be calculated by comparing the changes in enthalpy or entropy accompanying the following processes

(a) starting from crystalline components, A or B and A_qB_r are mixed together to form the corresponding eutectic mixture at the eutectic temperature, at which the eutectic mixture is molten.

(b) starting from crystalline components, A or B and A_qB_r are heated from the eutectic temperature to the temperature of their fusion, melted at this temperature, cooled to the eutectic temperature, and at this temperature are mixed together to form the melt of eutectic composition.

The enthalpy or entropy balance (the latter being obtained by the use of the Le Chatelier–Shreder equation applied to both components) yields the following relation for the heat of fusion for the eutectic

$$\begin{aligned}&\Delta H_{\mathrm{fus}}(\mathrm{eut}, T_{\mathrm{fus}}(\mathrm{eut}))\\&\quad = y(\mathrm{eut}, \mathrm{A\ or\ B})\Delta H_{\mathrm{fus}}(\mathrm{A\ or\ B}, T_{\mathrm{fus}}(\mathrm{eut}))\\&\qquad + y(\mathrm{eut}, \mathrm{A}_q\mathrm{B}_r)\left[\Delta H_{\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r, T_{\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r)) + \int_{T_{\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r)}^{T_{\mathrm{fus}}(\mathrm{eut})} \Delta C_{p,\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r, T)\,\mathrm{d}T\right]\\&\qquad + \Delta H_{\mathrm{mix,melt}}(\mathrm{eut}, T_{\mathrm{fus}}(\mathrm{eut}))\end{aligned} \tag{8}$$

where $y(\mathrm{eut}, \mathrm{Y})$ is the mole fraction of component Y in the $A–A_qB_r$ or $B–A_qB_r$ system.

If enthalpic quantities for the compound A_qB_r are not known, $\Delta H_{\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r, T_{\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r))$ in eqn. (8) is substituted by that in eqn. (4), and $\Delta C_{p,\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r, T)$ is calculated using Neumann–Kopp's rule. If the values for the enthalpy of mixing in the binary system A–B are for 1 mole of the mixture, it is necessary to calculate this enthalpy required to yield the eutectic melt in the $A–A_qB_r$ or $B–A_qB_r$ system by comparing the enthalpy balances of two reaction paths by direct mixing of the basic components A and B, and by mixing of the basic components A and B into the binary compound A_qB_r and by subsequent mixing of this compound with the remaining amount of the major component.

DISCUSSION

Application of derived relations to estimate the heats of fusion of binary compounds and eutectics

The values for all the thermodynamic quantities in eqns. (4) and (8) are not known in most binary systems. It is, however, possible to use simplified forms of these relations or of relation (7) to estimate the heats of fusion for binary compounds or binary eutectics (estimated quantities are denoted by ^ above the quantity).

In the case of estimating the heat of fusion for the binary compound, simplifying assumptions can be divided, according to eqn. (4), into three boundary groups:

(a) $\Delta H_{\mathrm{mix,melt}}(\mathrm{A}_q\mathrm{B}_r,\ T_{\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r)) = 0$
$\Delta S^{\mathrm{E}}_{\mathrm{mix,melt}}(\mathrm{A}_q\mathrm{B}_r,\ T_{\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r)) = 0$
$(\gamma(\mathrm{X}, \mathrm{melt}, T_{\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r)) = 1)$
(ideal solutions)

(b) $\Delta H_{\mathrm{mix,melt}}(\mathrm{A}_q\mathrm{B}_r,\ T_{\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r)) \neq 0$
$\Delta S^{\mathrm{E}}_{\mathrm{mix,melt}}(\mathrm{A}_q\mathrm{B}_r,\ T_{\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r)) = 0$
$(\gamma(\mathrm{X}, \mathrm{melt}, T_{\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r)) \neq 1)$
(regular solutions)

(c) $\Delta H_{\mathrm{mix,melt}}(\mathrm{A}_q\mathrm{B}_r,\ T_{\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r)) \neq 0$
$\Delta S^{\mathrm{E}}_{\mathrm{mix,melt}}(\mathrm{A}_q\mathrm{B}_r,\ T_{\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r)) \neq 0$
$(\gamma(\mathrm{X}, \mathrm{melt}, T_{\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r)) = 1 \text{ or } \neq 1)$

To estimate the heats of fusion for binary eutectics, eqn. (8) can be, in the first approximation, simplified if the following conditions are fulfilled

$$\Delta H_{\mathrm{mix,melt}}(\mathrm{eut},\ T_{\mathrm{fus}}(\mathrm{eut})) = 0 \tag{9a}$$

$$\Delta C_{p,\mathrm{fus}}(\mathrm{A}_q\mathrm{B}_r,\ T) = 0 \tag{9b}$$

The simplied eqns. (7) and (8), obtained on the basis of the simplifying assumptions (a), (b), (c), i.e. eqns. (9a) and (9b), were used to determine estimated heats of fusion for equimolar binary compounds in the Na_2SO_4–NaF, K_2SO_4–KF ($q = r = 1$) systems and estimated heats of fusion for eutectics in the Na_2SO_4–NaF · Na_2SO_4, NaF · Na_2SO_4–NaF, K_2SO_4–KF · K_2SO_4, and KF · K_2SO_4–KF systems. The values of the heats and temperatures of fusion for NaF, Na_2SO_4, KF, K_2SO_4 and the temperature dependences of the heat capacities for their crystalline and melt phases were taken from ref. 1. $\Delta H_{\mathrm{mix,melt}}(\mathrm{AB}, T_{\mathrm{fus}}(\mathrm{AB}))$ and $\Delta H_{\mathrm{mix,melt}}(\mathrm{eut}, T_{\mathrm{fus}}(\mathrm{eut}))$ were calculated using the data from ref. 2 assuming that they are independent of temperature. Activity coefficients for the components in the melt were calculated according to ref. 2. Esimated values of the heats of fusion for NaF · Na_2SO_4 and KF · K_2SO_4 can be compared with those measured by us [3, 4]. The compositions of the eutectics and their temperatures of fusion in the Na_2SO_4–NaF and K_2SO_4–KF systems were taken from ref. 5.

Estimations of the heats of fusion for the binary compounds and eutectics in both systems studied are presented in Tables 1–6. The relative errors of the estimations for the heats of fusion (Δ) for the binary compounds are related to the experimental values. The relative errors of the estimations for the heats of fusion for the eutectics are related to the values of these quantities calculated using experimentally determined heats of fusion for binary compounds and enthalpies of mixing for the corresponding eutectic composition.

As can be seen from Tables 1 and 2, the estimated heats of fusion for NaF · Na_2SO_4 and KF · K_2SO_4 are lower than the measured values, and the

TABLE 1

Estimated heats of fusion of $NaF \cdot Na_2SO_4$ at the temperature of fusion 1060 K ($\Delta\hat{H}_{fus}(NaF \cdot Na_2SO_4, 1060\ K)$) under the simplifying assumptions (a), (b), (c), see text ($\Delta H_{fus}(NaF \cdot Na_2SO_4, 1060\ K) = (69 \pm 4)\ kJ\ mol^{-1}$ [3])

	$\Delta H_{mix,melt}(NaF \cdot Na_2SO_4, 1060\ K)$/ kJ mol^{-1}	γ	$\Delta S^E_{mix,melt}(NaF \cdot Na_2SO_4, 1060\ K)$/ J mol^{-1} K^{-1}	$\Delta\hat{H}_{fus}(NaF \cdot Na_2SO_4, 1060\ K)$/ kJ mol^{-1}	Δ/ %
(a)	0	1	0	60	−13
(b)	2.78 [2]	$\neq 1$	0	60	−13
(c)	2.78 [2]	$\gamma(NaF) = 0.837$ $\gamma(Na_2SO_4) = 1.003$	4.08 [2]	64	−7

TABLE 2

Estimated heats of fusion of $KF \cdot K_2SO_4$ at the temperature of fusion 1148 K ($\Delta\hat{H}_{fus}(KF \cdot K_2SO_4, 1148\ K)$) under the simplifying assumptions (a) and (b) ($\Delta H_{fus}(KF \cdot K_2SO_4, 1148\ K) = (86 \pm 3)\ kJ\ mol^{-1}$ [4])

	$\Delta H_{mix,melt}(KF \cdot K_2SO_4, 1148\ K)$/ kJ mol^{-1}	γ	$\Delta S^E_{mix,melt}(KF \cdot K_2SO_4, 1148\ K)$/ J mol^{-1} K^{-1}	$\Delta\hat{H}_{fus}(KF \cdot K_2SO_4, 1148\ K)$/ kJ mol^{-1}	Δ/ %
(a)	0	1	0	75	−13
(b)	−2.58 [2]	$\neq 1$	0	75	−13

TABLE 3

Estimated heats of fusion of the eutectic in the Na_2SO_4–$NaF \cdot Na_2SO_4$ system at the eutectic temperature 1021 K [5] ($\Delta\hat{H}_{fus}$(eut, 1021 K)) for various values of input quantities

ΔH_{fus}, resp. $\Delta\hat{H}_{fus}$($NaF \cdot Na_2SO_4$, 1060 K)/ $kJ\,mol^{-1}$	$\Delta H_{mix,melt}$(eut, 1021 K)/ $kJ\,mol^{-1}$	$\Delta C_{p,fus}(Y)$ [a]/ $J\,mol^{-1}\,K^{-1}$	$\Delta\hat{H}_{fus}$(eut, 1021 K)/ $kJ\,mol^{-1}$	Δ/ %
69 [3]	0.36 [2]	≠0 [1]	41	
69 [3]	0	≠0 [1]	40	−2
69 [3]	0	0	40	−2
60	0	0	36	−12
64	0	0	38	−5

[a] Y is Na_2SO_4 or $NaF \cdot Na_2SO_4$ ($\Delta C_{p,fus}$($NaF \cdot Na_2SO_4$) according to Neumann–Kopp's rule).

TABLE 4

Estimated heats of fusion of the eutectic in the $NaF \cdot Na_2SO_4$–NaF system at the eutectic temperature 1054 K [5] ($\Delta\hat{H}_{fus}$(eut, 1054 K)) for various values of input quantities

ΔH_{fus}, resp. $\Delta\hat{H}_{fus}$($NaF \cdot Na_2SO_4$, 1060 K)/ $kJ\,mol^{-1}$	$\Delta H_{mix,melt}$(eut, 1054 K)/ $kJ\,mol^{-1}$	$\Delta C_{p,fus}(Y)$ [a]/ $J\,mol^{-1}\,K^{-1}$	$\Delta\hat{H}_{fus}$(eut, 1054 K)/ $kJ\,mol^{-1}$	Δ/ %
69 [3]	0.42 [2]	≠0 [1]	57	
69 [3]	0	≠0 [1]	57	0
69 [3]	0	0	58	2
60	0	0	52	−9
64	0	0	54	−2

[a] Y is $NaF \cdot Na_2SO_4$ or NaF ($\Delta C_{p,fus}$($NaF \cdot Na_2SO_4$) according to Neumann–Kopp's rule).

TABLE 5

Estimated heats of fusion of the eutectic in the K_2SO_4–$KF \cdot K_2SO_4$ system at the eutectic temperature 1143 K [5] ($\Delta\hat{H}_{fus}$(eut, 1143 K)) for various values of input quantities

ΔH_{fus}, resp. $\Delta\hat{H}_{fus}(KF \cdot K_2SO_4$, 1148 K)/ kJ mol^{-1}	$\Delta H_{mix,melt}$(eut, 1143 K)/ kJ mol^{-1}	$\Delta C_{p,fus}(Y)$ [a]/ J mol^{-1} K^{-1}	$\Delta\hat{H}_{fus}$(eut, 1143 K)/ kJ mol^{-1}	Δ/ %
86 [4]	−0.18 [2]	≠0 [1]	73	
86 [4]	0	≠0 [1]	73	0
86 [4]	0	0	72	−1
75	0	0	64	−12

[a] Y is K_2SO_4 or $KF \cdot K_2SO_4$ ($\Delta C_{p,fus}(KF \cdot K_2SO_4)$ according to Neumann–Kopp's rule).

TABLE 6

Estimated heats of fusion of the eutectic in the $KF \cdot K_2SO_4$–KF system at the eutectic temperature 1051 K [5] ($\Delta\hat{H}_{fus}$(eut, 1051 K)) for various values of input quantities

ΔH_{fus}, resp. $\Delta\hat{H}_{fus}(KF \cdot K_2SO_4$, 1148 K)/ kJ mol^{-1}	$\Delta H_{mix,melt}$(eut, 1051 K)/ kJ mol^{-1}	$\Delta C_{p,fus}(Y)$ [a]/ J mol^{-1} K^{-1}	$\Delta\hat{H}_{fus}$(eut, 1051 K)/ kJ mol^{-1}	Δ/ %
86 [4]	−0.61 [2]	≠0 [1]	39	
86 [4]	0	≠0 [1]	39	0
86 [4]	0	0	40	3
75	0	0	38	−3

[a] Y is $KF \cdot K_2SO_4$ or KF ($\Delta C_{p,fus}(KF \cdot K_2SO_4)$ according to Neumann–Kopp's rule).

absolute values of their relative errors are within the limits 7–13%. This difference is probably due to the limited validity of the Neumann–Kopp rule which, in most cases, yields higher values of $C_{p,\mathrm{cr}}(\mathrm{A}_q\mathrm{B}_r, T)$ in eqn. (4).

The first three lines in Tables 3–6 imply that zero values of $\Delta H_{\mathrm{mix,melt}}(\mathrm{eut}, T_{\mathrm{fus}}(\mathrm{eut}))$ and $\Delta C_{p,\mathrm{fus}}(\mathrm{Y})$, considered in the estimation of the heats of fusion for eutectics in the systems under study, have very low influence on the values of $\Delta \hat{H}_{\mathrm{fus}}(\mathrm{eut}, T_{\mathrm{fus}}(\mathrm{eut}))$. Absolute values of their relative errors are within the limits 0–12%.

The confidence of the above-mentioned ways of estimating these quantities depends, in general, on the selection of simplifying conditions as well as on the mutual position of the points of fusion for double compounds or components and eutectic points.

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