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Determination of the enthalpy of fusion of $NaMgF_3$ and $KMgF_3$

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Abstract

The enthalpy of melting of $NaMgF_3$ and $KMgF_3$ at the dystectic temperature of fusion of these compounds was determined using a high-temperature calorimeter, the Setaram HTC 1800 K. It was found that $\Delta_{fus}H_m(NaMgF_3;\ 1303\ K) = (66 \pm 4)\ kJ\ mol^{-1}$ and $\Delta_{fus}H_m(KMgF_3;\ 1343\ K) = (96 \pm 5)\ kJ\ mol^{-1}$. The given error is calculated at the level of reliability $(1 - \alpha) = 0.95$.

Keywords: Heat of fusion; Mixed salt; Potassium magnesium fluoride; Sodium magnesium fluoride

1. Introduction

Magnesium fluoride may be considered as a promising additive to the bath of the Hall–Héroult process [1]. Sokolov and Belyaev [2] and Kostyukov et al. [3] have assumed that magnesium fluoride is present in cryolite-based melts in the form of anions MgF_3^-. The formation of these complex anions influences the activity of aluminium complexes in the melt.

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This work presents the results of the calorimetric determination of the enthalpy of fusion of the binary compounds $NaMgF_3$ and $KMgF_3$. This parameter is required for calculation of a reliable evaluation of the degree of thermal dissociation of these compounds and estimation of the amount of MgF_3^- anions present in the melt. Both compounds have a dystectic melting point.

2. Experimental

Samples of $NaMgF_3$ and $KMgF_3$ were prepared by melting equimolar amounts of NaF and KF, respectively, with MgF_2 in a platinum crucible. All chemicals were of "pro analysis" grade (Lachema). KF was dried in a vacuum furnace for 24 h in the presence of P_2O_5 and then at gradually increasing temperatures up to 150°C for another 10 h.

The enthalpy of the solid–liquid phase transition was determined using a high-temperature calorimeter, the Setaram HTC 1800 K, working in the DSC mode. A detailed description of the experimental procedure can be found elsewhere [4].

In this work, a rate of change of temperature of 1 K min^{-1} was used. K_2SO_4 was used for calibration. Samples of $NaMgF_3$ (250.83 mg), of $KMgF_3$ (250.29 mg) and K_2SO_4 (250.33 mg), respectively, were sealed in platinum crucibles. The crucible containing the investigated substance or K_2SO_4 was placed in the upper sintered alumina crucible of the calorimeter. The lower crucible of the calorimeter was filled with small pieces of sintered alumina (corundum) placed in a platinum crucible. The melting temperature of the calibration material (1069°C) is close to the melting temperatures of both investigated substances: $\theta_{fus}(NaMgF_3) = 1030°C$, $\theta_{fus}(KMgF_3) = 1070°C$. The heat flow between the crucibles is proportional to the temperature difference between them.

3. Results and discussion

The electric signal from the thermocouples corresponding to the temperature difference between the two crucibles was treated by the modified procedure proposed by Guttman and Flynn [5]. This procedure is based on a non-isothermal Hess law. The assumptions involved in this method of data treatment have previously been discussed in detail [4]. Corrections to the values of Q_{fus}/λ_{fus} and $Q_{cryst}/\lambda_{cryst}$ with respect to the equilibrium temperatures of fusion were not carried out because it is assumed that the contribution of the heat resulting from the difference in the heat capacities of the solid and liquid phase (which can be estimated on the basis of Kirchhoff's law) is lower than the error of the method used. (In the above, Q_{fus} and Q_{cryst} are the heat effects of melting and of crystallization of the sample, and λ_{fus} and λ_{cryst} are the corresponding coefficients of heat transfer between the crucibles.)

Because the temperatures of phase transition of the investigated substances and of the salt used for calibration are close, the assumption that λ_{fus} and λ_{cryst} are the same for both salts is fulfilled. It follows that the enthalpy of phase transition of the investigated substance X is related to the enthalpy of phase transition of K_2SO_4 used as calibration substance by the relationship

$$\frac{\left(\dfrac{Q_{\mathrm{trans}}(\mathrm{X})}{\lambda_{\mathrm{trans}}}\right)_{\Phi}\dfrac{1}{m(\mathrm{X})}}{\left(\dfrac{Q_{\mathrm{trans}}(\mathrm{calib})}{\lambda_{\mathrm{trans}}}\right)_{\Phi}\dfrac{1}{m(\mathrm{calib})}} = \kappa_{\mathrm{trans}} = \frac{\Delta_{\mathrm{trans}}h(\mathrm{X})}{\Delta_{\mathrm{trans}}h(\mathrm{calib})} \tag{1}$$

where the subscript trans denotes melting or crystallization, Φ denotes the arithmetic mean, m is the mass of sample, h is the specific enthalpy of the phase transition, and X is $NaMgF_3$ or $KMgF_3$.

Experimentally obtained values of $Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}}$ and $Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}}$, with their arithmetic means and the errors in their determination, are presented in Tables 1 and 2. Errors in the arithmetic means of these quantities were calculated using the Student distribution at the level of reliability of $(1-\alpha)=0.95$.

Introducing into Eq. (1) the experimental data presented in Tables 1 and 2 and the mass of samples, we obtain

$$\kappa_{\mathrm{fus}}(\mathrm{NaMgF_3}) = (2.927 \pm 0.141); \quad \kappa_{\mathrm{cryst}}(\mathrm{NaMgF_3}) = (3.071 \pm 0.182)$$

The arithmetic mean of these values equals

$$\kappa_{\Phi} = (2.999 \pm 0.161) \tag{2}$$

Then, for the specific enthalpy of fusion of $NaMgF_3$, we obtain

$$\Delta_{\mathrm{fus}}h(\mathrm{NaMgF_3}) = \kappa_{\Phi}(\mathrm{NaMgF_3})\Delta_{\mathrm{fus}}h(\mathrm{K_2SO_4}) = (634 \pm 34)\ \mathrm{kJ\ kg^{-1}} \tag{3}$$

(The value of $\Delta_{\mathrm{fus}}h(\mathrm{K_2SO_4}) = 211\ \mathrm{kJ\ kg^{-1}}$ was taken from ref. 6.) The error in κ and thus in $\Delta_{\mathrm{fus}}h(\mathrm{NaMgF_3})$ was determined using the Gauss law of propagation of errors.

Table 1
Experimental values of $Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}}$ and $(Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}})_{\Phi}$ for $NaMgF_3$, $KMgF_3$ and K_2SO_4

Sample	$(Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}})/(\mathrm{K\ s})$					$(Q_{\mathrm{fus}}/\lambda_{\mathrm{fus}})_{\Phi}/(\mathrm{K\ s})$
$NaMgF_3$	560	541	568	572	591	566 ± 23
$KMgF_3$	730	727	735	706	711	722 ± 16
K_2SO_4	198	191	195	187	192	193 ± 5

Table 2
Experimental values of $Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}}$ and $(Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}})_{\Phi}$ for $NaMgF_3$, $KMgF_3$ and K_2SO_4

Sample	$(Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}})/(\mathrm{K\ s})$					$(Q_{\mathrm{cryst}}/\lambda_{\mathrm{cryst}})_{\Phi}/(\mathrm{K\ s})$
$NaMgF_3$	677	676	680	680	674	677 ± 3
$KMgF_3$	826	852	826	852	833	838 ± 16
K_2SO_4	207	231	211	221	230	220 ± 13

The molar enthalpy and entropy of fusion of $NaMgF_3$ at the temperature of melting $T_{\mathrm{fus}} = 1303$ K were found to be

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}}(\mathrm{NaMgF_3}) = (66 \pm 4)\ \mathrm{kJ\ mol^{-1}} \tag{4}$$

$$\Delta_{\mathrm{fus}}S_{\mathrm{m}}(\mathrm{NaMgF_3}) = (51 \pm 3)\ \mathrm{J\ mol^{-1}\ K^{-1}} \tag{5}$$

The enthalpy of fusion of $KMgF_3$ was determined using the same procedure as that described above. The experimental data used for the calculation are presented in Tables 1 and 2. After introducing these data into Eq. (1) we obtain

$$\kappa_{\mathrm{fus}}(\mathrm{KMgF_3}) = (3.742 \pm 0.127); \quad \kappa_{\mathrm{cryst}}(\mathrm{KMgF_3}) = (3.810 \pm 0.236)$$

The arithmetic mean of these values equals

$$\kappa_{\Phi}(\mathrm{KMgF_3}) = (3.776 \pm 0.182) \tag{6}$$

Then, for the specific enthalpy of fusion of $KMgF_3$, we obtain

$$\Delta_{\mathrm{fus}}h(\mathrm{KMgF_3}) = (798 \pm 38)\ \mathrm{kJ\ kg^{-1}} \tag{7}$$

The molar enthalpy and entropy of fusion of $KMgF_3$ at the temperature of melting $T_{\mathrm{fus}} = 1343$ K were found to be

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}}(\mathrm{KMgF_3}) = (96 \pm 5)\ \mathrm{kJ\ mol^{-1}} \tag{8}$$

$$\Delta_{\mathrm{fus}}S_{\mathrm{m}}(\mathrm{KMgF_3}) = (72 \pm 3)\ \mathrm{J\ mol^{-1}\ K^{-1}} \tag{9}$$

4. References

[1] K. Grjotheim, H. Kvande and K. Matiašovský, Light Metals, (1983) 397.

[2] O.K. Sokolov and A.I. Belyaev, Izv. Vyssh. Uchebn. Zaved., Tsvetn. Metall., 3 (1960) 72.

[3] A.A. Kostyukov, N.Y. Anufrieva, Z.I. Balashova and V.I. Savinov, Light Metals, (1983) 389.

[4] K. Adamkovičová, P. Fellner, L. Kosa, P. Lazor, I. Nerád and I. Proks, Thermochim. Acta, 191 (1991) 57.

[5] C.M. Guttman and J.H. Flynn, Anal. Chem., 45(2) (1973) 408.

[6] I. Barin and O. Knacke, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Verlag Stahleisen GmbH, Düsseldorf, 1973, p. 379.