

# Thermodynamic properties of some molten alkaline fluoride—beryllium fluoride mixtures\*

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The enthalpies of fusion of both  $\text{Li}_2\text{BeF}_4$  and  $\text{Na}_2\text{BeF}_4$  have been measured and the values of 41.9 and 25.5 kJ mol<sup>-1</sup>, respectively, have been found. The equations for the partial enthalpy of mixing, partial excess Gibbs free energy, and partial excess entropy (in all cases at 1135 K) for the  $\text{BeF}_2$  as well as for the LiF side have been derived.

The integral excess quantities of mixing for molten LiF— $\text{BeF}_2$  mixtures have been calculated. The structural reasons for the obtained values of the studied thermodynamic quantities have been discussed.

Были измерены энтальпии плавления  $\text{Li}_2\text{BeF}_4$  и  $\text{Na}_2\text{BeF}_4$  и найдены величины 41,9 · 10<sup>3</sup> Дж моль и 25,5 · 10<sup>3</sup> Дж моль соответственно. Были получены уравнения для парциальной энтальпии смешивания, для парциальной избыточной энергии Гиббса и для парциальной избыточной энтропии во всех случаях при 1135 К как для стороны  $\text{BeF}_2$ , так и для стороны LiF.

Были рассчитаны интегральные избыточные величины смешивания для расплавленных смесей LiF— $\text{BeF}_2$ . Причины структурного характера для найденных значений, изучаемых термодинамических величин, были дискутированы.

The fluoride mixtures NaF— $\text{MF}_2$  (M = alkaline earth metal), LiF— $\text{AlF}_3$ , and NaF— $\text{AlF}_3$  belong to the class of mixtures called charge-unsymmetrical mixtures. This type of mixtures was discussed by the present author [1, 2]. He correlated the interaction parameter

$$b = (\bar{G}_1^E/N_2^2)_{N_2=0}$$

with an empirical parameter

$$\left( \frac{\frac{r_+}{1} - \frac{r_{++}}{2}}{d_1 + d_2} \right)^2$$

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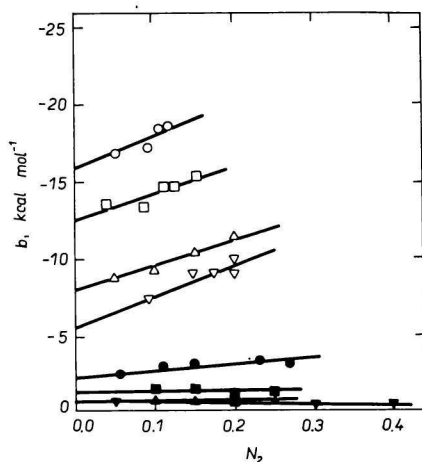


Fig. 1a. The interaction parameter  $b$  as a function of the parameter  $(r_+ - r_{++}/2)(d_1 + d_2)$ .  
 ○ NaF—AlF<sub>3</sub>; □ LiF—AlF<sub>3</sub>; △ NaF—BeF<sub>2</sub>;  
 ▽ NaF—MgF<sub>2</sub>; ● NaF—CaF<sub>2</sub>; ■ NaF—SrF<sub>2</sub>;  
 ▲ NaF—BaF<sub>2</sub>; ▼ NaF—LiF.

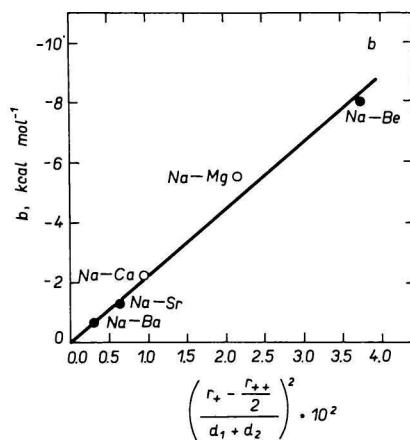


Fig. 1b. The interaction parameter  $b = \bar{G}_1^E/N_2^2$  plotted as a function of composition.

and found a linear dependence between  $b$  and the latter parameter, as shown in Figs. 1a, b. Here  $r_+$  is the radius of the univalent ion and  $r_{++}$  the radius of the divalent ion, while  $d_1$  and  $d_2$  are the sums of the radii of the cation and the fluoride ion. It was pointed out that the interaction parameter,  $b$ , could be obtained by extrapolating  $\bar{G}_1^E/N_2^2$  to  $N_2=0$ . When this was done for different mixtures with a common salt (sodium fluoride), interaction parameters which referred to the same temperature and composition were obtained. It is important in charge-unsymmetrical mixtures to avoid the asymmetry effect (concentration dependence) as well as the temperature dependence of the Gibbs free energy of mixing.

Davis [3] extended the conformal ionic solution theory for the simple AX—BX mixtures to the more complicated charge-unsymmetrical mixtures. In his evaluation it was predicted that the limiting excess Gibbs free energy and the limiting enthalpy in their first approximation should have the form

$$\lim_{N \rightarrow 0} \frac{\Delta A^E}{N(1-N)} = B + C\delta_{12},$$

where  $\Delta A^E$  is the excess Gibbs free energy or the enthalpy,  $N$  the mole fraction of the divalent salt,  $\delta_{12}$  the conformal solution parameter

$$\delta_{12} = \frac{d_1 - d_2}{d_1 d_2}$$

and  $B$  and  $C$  are unevaluated complicated integrals containing temperature and pressure dependence. These functions are different for the Gibbs free energy and the enthalpy. In his evaluation Davis [3] also refers to a reference salt, that is a common salt with a fixed cation—anion distance. Thus, according to the theory

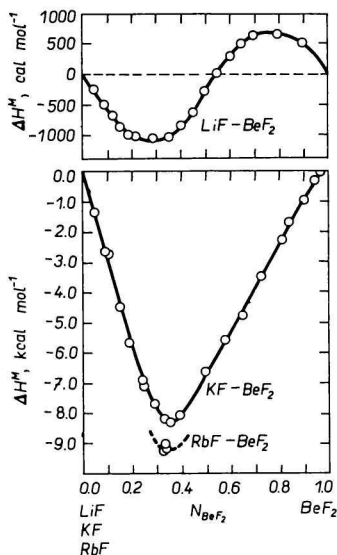


Fig. 2. Integral enthalpies in liquid mixtures of  $\text{BeF}_2$  with  $\text{LiF}$ ,  $\text{KF}$ , and  $\text{RbF}$ .

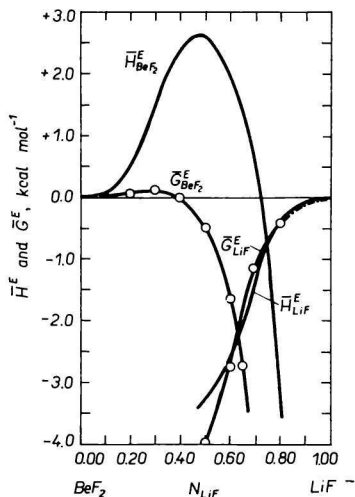


Fig. 3. Partial excess Gibbs free energies and excess enthalpies of mixing of  $\text{LiF}$  and  $\text{BeF}_2$  at  $862^\circ\text{C}$ .

Dash-dotted curve,  $\bar{H}_{\text{LiF}}^E$  from eqn (8).

one should obtain a linear dependence between the limiting values of  $\Delta A^E$  for a group of mixtures with a common salt when the interaction parameter is plotted vs.

$$\delta_{12} = \frac{d_1 - d_{\text{ref}}}{d_1 d_{\text{ref}}}$$

$d_{\text{ref}}$ , the cation—anion distance in the reference salt, is called the reference length.

It has been shown by the present author [4] that the above expression is too simple and that higher order terms must be included in the expressions for the excess thermodynamic properties of complex mixtures of the same type as  $\text{AlkCl—MgCl}_2$ . These equations should be given in the general form

$$\Delta A^E = N(1 - N) (B + C\delta_{12} + D\delta_{12}^2 + \dots)$$

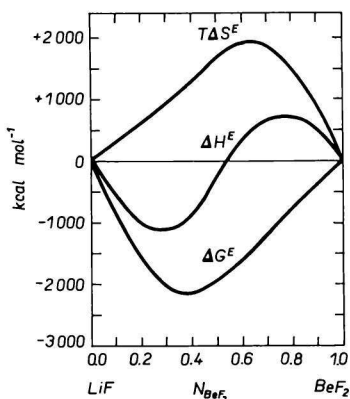


Fig. 4. Integral Gibbs free energy, enthalpy, and entropy of mixing for liquid mixtures of LiF and BeF<sub>2</sub>.

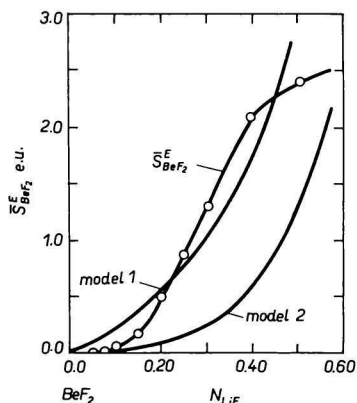


Fig. 5. Partial excess entropies of BeF<sub>2</sub> in liquid mixtures of BeF<sub>2</sub> with LiF. The excess entropy values are compared with values derived from models proposed in [10].

Here  $B$  and  $C$  are functions of temperature  $T$ , pressure  $P$ , and length parameter  $d_{\text{ref}}$ , while  $D$  is a function of  $T$ ,  $P$ ,  $d_{\text{ref}}$ , and also of composition.

## Results

The phase diagram of the system LiF—BeF<sub>2</sub>, and the phase equilibria in this system, have recently been re-investigated by Romberger *et al.* [5], who for the first time established Li<sub>2</sub>BeF<sub>4</sub> as a congruently melting compound with a phenacite (Be<sub>2</sub>SiO<sub>4</sub>)-type structure. This system also contains the compound LiBeF<sub>3</sub>, which disproportionates in the solid state at 563 K to Li<sub>2</sub>BeF<sub>4</sub> and BeF<sub>2</sub>.

### 1. Enthalpies of fusion

The enthalpies of fusion of both Li<sub>2</sub>BeF<sub>4</sub> and Na<sub>2</sub>BeF<sub>4</sub> have been measured by Holm, Jenssen-Holm, and Grønvald [6].

In the case of Li<sub>2</sub>BeF<sub>4</sub> the following result was obtained

$$\Delta H_f = (-336 + 14.06 T) \text{ cal mol}^{-1}, \text{ i.e. } (-1406 + 58.83 T) \text{ J mol}^{-1} \quad (1)$$

corresponding to  $\Delta H_f = (10.0 \pm 0.1) \text{ kcal mol}^{-1}$ , i.e.  $(41.8 \pm 0.4) \text{ kJ mol}^{-1}$  at the melting point 723.1 K.

In the case of Na<sub>2</sub>BeF<sub>4</sub> the results were fitted to the equation

$$\Delta H_f = (-9735 + 18.32 T) \text{ cal mol}^{-1}, \text{ i.e. } (-40\,731 + 76.65 T) \text{ J mol}^{-1} \quad (2)$$

corresponding to  $\Delta H_f = (6.1 \pm 0.2) \text{ kcal mol}^{-1}$ , i.e.  $(25.5 \pm 0.8) \text{ kJ mol}^{-1}$  at the melting point 832 K.

\* 1 cal = 4.1840 J.

As can be seen this value is about  $4 \text{ kcal mol}^{-1}$ , i.e.  $16.7 \text{ kJ mol}^{-1}$  lower than the enthalpy of fusion of  $\text{Li}_2\text{BeF}_4$ . This is mainly due to the fact that in the phenacite structure the  $\text{Li}^+$  ions are coordinated by 4  $\text{F}^-$  ions from the  $\text{BeF}_4^{2-}$  groups, while  $\text{Na}_2\text{BeF}_4$  has the sodium sulfate structure with  $\text{Na}^+$  coordinated by 6  $\text{F}^-$  from the  $\text{BeF}_4^{2-}$  groups.

## 2. Integral enthalpies of mixing

Integral enthalpies of mixing for liquid mixtures of alkali fluorides with  $\text{BeF}_2$  have been measured by Holm and Kleppa [7] at 1135 K. Their results are given in Fig. 2.

The enthalpy data were fitted by the present author to the polynomial expansion

$$\Delta H^M = N(1-N)(a + bN + cN^2 + dN^3), \quad (3)$$

where  $N$  is the mole fraction of  $\text{BeF}_2$  and  $a, b, c, d$  are constants. The results obtained for the two systems are given in Table 1.

The only positive term is the  $c$  term. Thus, it is obvious that this term is responsible for the positive contribution to the enthalpy of mixing. This term can be attributed to the break-down of the fluorine network when an alkali fluoride is added to molten beryllium fluoride. In the calculation of the partial enthalpy of mixing at 1135 K the following equation, obtained by derivation of eqn (3), has been used

$$\begin{aligned} \bar{H}_{\text{BeF}_2}^E = & (-4.34 - 52.38N + 280.11N^2 - 232.32N^3)(1-N)^2 \text{ kcal mol}^{-1} \\ & (-18.16 - 219.16N + 1171.98N^2 - 972.03N^3)(1-N)^2 \text{ kJ mol}^{-1} \end{aligned} \quad (4)$$

where  $N$  is the mole fraction of  $\text{BeF}_2$  in the mixture.

From the data given by Hitch and Baes [8] the partial excess Gibbs free energy of  $\text{BeF}_2$  at 1135 K can be expressed directly as follows

$$\begin{aligned} \bar{G}_{\text{BeF}_2}^E = & (-10.10 + 37.80N - 45.60N^2 + 20.70N^3)(1-N)^2 \text{ kcal mol}^{-1} \\ & (-42.26 + 158.16N - 190.79N^2 + 86.61N^3)(1-N)^2 \text{ kJ mol}^{-1} \end{aligned} \quad (5)$$

The enthalpy and free energy data are plotted in Fig. 3.

From the difference between eqn (4) and eqn (5) it is possible to express the partial excess entropy of  $\text{BeF}_2$  as a function of composition at 1135 K

$$\begin{aligned} \bar{S}_{\text{BeF}_2}^E = & (5.07 - 79.5N + 287.0N^2 - 222.9N^3)(1-N)^2 \text{ cal mol}^{-1} \text{ K}, \\ & (21.21 - 332.63N + 1200.8N^2 - 932.6N^3)(1-N)^2 \text{ J mol}^{-1} \text{ K}. \end{aligned} \quad (6)$$

Table 1  
Summary of enthalpy of mixing data in  $\text{AlkF}-\text{BeF}_2$  systems

System	$a$	$b$	$c$	$d$	
(Li—Be)F	- 4.34	- 26.19	+ 93.73	- 58.08	kcal mol <sup>-1</sup>
(K—Be)F	-23.17	-109.65	+ 256.70	-129.38	
(Li—Be)F	-18.17	-109.65	+ 392.43	-243.17	
(K—Be)F	-97.01	-459.08	+ 1074.75	-541.69	kJ mol <sup>-1</sup>

The entropy data are plotted in Fig. 3.

#### The LiF-side

By derivation of eqn (3) one obtains the following expression for the partial excess enthalpy of LiF

$$\begin{aligned}\bar{H}_{\text{LiF}} = & (21.85 - 239.12 N + 454.35 N^2 - 232.32 N^3) N^2 \text{ kcal mol}^{-1} \\ & (91.42 - 1000.5 N + 1901.00 N^2 - 972.03 N^3) N^2 \text{ kJ mol}^{-1}\end{aligned}\quad (7)$$

This equation, however, does not give the best fit between the experimental and the calculated data for the concentration range 0–15 mole % BeF<sub>2</sub>. In this range eqn (8) is recommended

$$\begin{aligned}\bar{H}_{\text{LiF}} = & (-3.715 - 33.45 N + 97.79 N^2) N^2 \text{ kcal mol}^{-1} \\ & (-15.544 - 139.95 N + 409.15 N^2) N^2 \text{ kJ mol}^{-1}\end{aligned}\quad (8)$$

The freezing point data given by *Braunstein, Romberger, and Ezell* [9] and the Gibbs free energy data given by *Hitch and Baes* [8] were used to calculate the partial excess Gibbs free energy of LiF in the mixture. These data are plotted in Fig. 3. A least squares treatment of these data gives

$$\begin{aligned}\bar{G}_{\text{LiF}}^E = & (-3.711 - 21.570 N - 27.294 N^2) N^2 \text{ kcal mol}^{-1} \\ & (-15.527 - 90.245 N - 114.198 N^2) N^2 \text{ kJ mol}^{-1}\end{aligned}\quad (9)$$

The partial excess entropy of LiF at 1135 K is given by the difference between eqns (7) and (8)

$$\begin{aligned}\bar{S}_{\text{LiF}}^E = & (-11.88 + 125.08 N) N^3 \text{ cal mol}^{-1} \text{ K}^{-1}, \\ & (-49.71 + 523.33 N) N^3 \text{ J mol}^{-1} \text{ K}^{-1}.\end{aligned}\quad (10)$$

The partial excess Gibbs free energies given by *Hitch and Baes* [8] have been fitted to eqn (11) which is less complex than eqn (5)

$$\begin{aligned}\bar{G}_{\text{BeF}_2}^E = & (-21.220 + 54.193 N - 31.712 N^2) (1 - N)^2 \text{ kcal mol}^{-1} \\ & (-88.784 + 226.744 N - 132.683 N^2) (1 - N)^2 \text{ kJ mol}^{-1}\end{aligned}\quad (11)$$

$N$  is the mole fraction of BeF<sub>2</sub> in the mixture.

Since the partial excess Gibbs free energy of LiF in the system is also known, eqn (9), it is possible to derive the integral excess Gibbs free energy of mixing from the Gibbs–Duhem relation.

The integral excess enthalpy, excess Gibbs free energy, and excess entropy of mixing for molten LiF–BeF<sub>2</sub> mixtures at 1135 K are plotted in Fig. 4.

## Discussion

From Fig. 4 it can be seen that the entropy term is the dominating one and determines both the sign and the magnitude of the deviation from ideality. The excess entropy is of the same order of magnitude as the ideal configurational entropy

$$\Delta S^M = -R[N \ln N + (1 - N) \ln (1 - N)] \quad (12)$$

In the paper [7] the partial entropy of mixing of BeF<sub>2</sub> was discussed with reference to two models for liquid BeF<sub>2</sub> originally proposed by *Førland* [10]. A mixture of BeF<sub>2</sub> and an alkali fluoride will contain two types of fluoride ions

— those attached to a single beryllium ion ( $-F$ ) and those which are attached to two beryllium ions, forming one of the fluorine bridges in the network structure ( $-F-$ ).

If the bridging and non-bridging fluoride ions are randomly distributed, the following expression for the partial entropy of beryllium fluoride is valid:

*Model 1*

$$\Delta \bar{S}_{\text{BeF}_2} = -2R \ln \left[ \left( 1 - \frac{3}{2} N_{\text{LiF}} \right) / \left( 1 - \frac{1}{2} N_{\text{LiF}} \right) \right] \quad (13)$$

If the bridging fluoride ions occur in pairs the following expression is valid:

*Model 2*

$$\Delta \bar{S}_{\text{BeF}_2} = -2R \ln \left[ \left( 1 - \frac{3}{2} N_{\text{LiF}} \right) / \left( 1 - N_{\text{LiF}} \right) \right] \quad (14)$$

The two theoretical entropy curves are compared with the experimental curve in Fig. 5. As can be seen a somewhat different picture is obtained from what was presented in the original paper by *Holm* and *Kleppa* [7]. The calculated experimental curve in Fig. 5 is based on Gibbs free energy data and enthalpy data at the same temperature, 862°C, while in the original paper Gibbs free energy data at 800°C were used. The plot in Fig. 5 shows, as should be expected, that the partial excess entropy curve starts from  $\bar{S}_{\text{BeF}_2}^E = 0$ , *i.e.*, ideal entropy of mixing, at very low concentrations of LiF, and then shows increasingly positive partial excess entropies at higher contents of LiF.

It may be justified to ask, however, whether a discussion of the structure of the melt which is based on simplified models and entropy data which may not at all be configurational, warrant the space devoted to it. The best model according to [10] gives an enthalpy of fusion for  $\text{BeF}_2$  of 9.7 kcal mol<sup>-1</sup> (40.58 kJ mol<sup>-1</sup>), while the calorimetric value given [11] is 1.1 kcal mol<sup>-1</sup> (4.60 kJ mol<sup>-1</sup>). As has been pointed out by this author [12], this clearly demonstrates that evaluation of "entropy models" from Gibbs free energy data by simply disregarding the enthalpy term can, and often will, lead to directly misleading results even in diluted mixtures.

A better treatment of the entropy data in these types of mixtures would probably be to look for a correlation between the excess entropy and the excess enthalpy of mixing for a group of binary mixtures of the same type. For example, in his analysis of the excess entropies in the  $\text{AlkCl}-\text{MgCl}_2$  mixtures, the present author [13] plotted  $\Delta S^E$  vs.  $\Delta H^E$  and found nearly a linear dependence between the two excess functions. It was suggested that the configurational part of the excess entropy could be divided into two principal parts

$$\Delta S^E = \Delta S_1^E + \Delta S_2^E$$

Table 2

Partial excess Gibbs free energy of KF in molten KF—BeF<sub>2</sub> mixtures

Composition $N_{\text{BeF}_2}$	$T_f$ K	$\bar{G}^E/N_{\text{BeF}_2}$	
		kcal mol <sup>-1</sup>	kJ mol <sup>-1</sup>
0.000	1130.2	—	—
0.1270	1028.4	-20.3	- 85.0
0.1505	982.4	-24.1	-100.9

The first of these effects,  $\Delta S_1^E$ , is due to a reduction in the number of independent units in the system, which results in a negative contribution and is the major factor in the case of very strong association. The introduction of a new species will make a positive contribution,  $\Delta S_2^E$ , and this term will be the controlling factor when the association is feeble, *i.e.*, in systems where the enthalpy of mixing is weakly negative, or positive.

A similar analysis of the AlkF—BeF<sub>2</sub> systems would be of great value, but since Gibbs free energy data for the systems NaF—BeF<sub>2</sub>, KF—BeF<sub>2</sub>, RbF—BeF<sub>2</sub>, and CsF—BeF<sub>2</sub> are not available, this is not possible at the present stage. However, one may obtain some information by comparing the enthalpy of mixing data with partial excess free energy data calculated from freezing point depressions on the KF-side of the system KF—BeF<sub>2</sub>. These data are given in Table 2.

As can be seen the interaction parameter based on Gibbs free energy data is of the order of -20 to -24 kcal mol<sup>-1</sup> (-84 to -100 kJ mol<sup>-1</sup>), while the corresponding interaction parameter for the enthalpy of mixing is -30 to -35 kcal mol<sup>-1</sup> (-126 to -146 kJ mol<sup>-1</sup>) in the same concentration range. This means, contrary to what was found in the LiF—BeF<sub>2</sub> system, that the enthalpy and not the entropy, determines the deviation from ideality. Since the enthalpy is more negative than the excess Gibbs free energy, the excess entropy of mixing will be negative in the KF—BeF<sub>2</sub> system.

It may therefore be justified to say that in AlkF—BeF<sub>2</sub> systems there will be two major contributions to the entropy of mixing:

1. The break-down of the BeF<sub>2</sub> network will lead to a positive excess entropy of mixing.
2. Complex formation or tendencies to strong association of the species in the melt leads to a negative excess entropy of mixing.

The excess entropy of mixing, whether it is positive or negative, will always be a result of a compromise between these two main effects. In the LiF—BeF<sub>2</sub> system the first effect is the major one, and therefore the excess entropy in this system is positive.



## References

1. Holm, J. L., *Lic.Thesis*. The Technical University of Norway, Trondheim, 1963.
2. Holm, J. L., *Electrochim. Acta* **11**, 351 (1966).
3. Davis, H. T., *J. Chem. Phys.* **41**, 2761 (1964).
4. Holm, J. L., *Dr.Thesis*. The Technical University of Norway, Trondheim, 1971.
5. Romberger, K. A., Braunstein, J., and Thoma, R. E., *J. Phys. Chem.* **76**, 1154 (1972).
6. Holm, J. L., Jenssen-Holm, B., and Grønvd, F., *Acta Chem. Scand.* **27**, 2035 (1973).
7. Holm, J. L. and Kleppa, O. J., *Inorg. Chem.* **8**, 207 (1969).
8. Hitch, B. F. and Baes, C. F., Jr., *Inorg. Chem.* **8**, 201 (1969).
9. Braunstein, J., Romberger, K. A., and Ezell, R., private communication.
10. Førlund, T., in *Fused Salts*. (B. R. Sundheim, Editor.) P. 156. McGraw-Hill, New York, 1964.
11. Stull, D. R. and Prophet, H., *JANAF Thermochemical Tables*, 2nd Ed., Natl. Bur. Stand. (USA); Coden: NSRDA, 1971.
12. Holm, J. L., *Thermochim. Acta* **7**, 293 (1973).
13. Holm, J. L., *Acta Chem. Scand.* **23**, 1841 (1969).