

Cryometric determination of the enthalpy of fusion of sodium cryolite

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Using the method of classical thermal analysis a part of the liquidus of sodium cryolite in the system $\text{Na}_3\text{AlF}_6\text{—Na}_3\text{FSO}_4$ was measured in the composition range 0—5 mole % Na_3FSO_4 . On the basis of these results the molar enthalpy of fusion of cryolite was calculated. It was found that $\Delta H_f(\text{Na}_3\text{AlF}_6) = 115.4 \text{ kJ mol}^{-1}$; error in this result was estimated to be $\pm 4.9 \%$.

Методом классического термического анализа измерена часть ликвидуса натриевого криолита в системе $\text{Na}_3\text{AlF}_6\text{—Na}_3\text{FSO}_4$ в интервале концентраций 0—5 мол. % Na_3FSO_4 . На основании этих результатов рассчитана мольная энтальпия плавления криолита. Найдено, что $\Delta H_f(\text{Na}_3\text{AlF}_6) = 115,4 \text{ кДж моль}^{-1}$; точность этого результата $\pm 4,9 \%$.

Literature survey and theoretical

Knowledge of the enthalpy of fusion of sodium hexafluoroaluminate Na_3AlF_6 (cryolite) is important both from theoretical and practical points of view. For example, it is needed at calculation of the thermal and energy balance and/or the thermal inertia of aluminium cells (the electrolyte contains about 90 mass % of Na_3AlF_6).

The most precise values of the molar enthalpy of fusion $\Delta H_f(i)$ of chemical substances can be generally obtained from calorimetric measurements. However, when we deal with substances having higher melting temperature and which are also unstable and very corrosive the calorimetric determination of the quantity $\Delta H_f(i)$ can be less reliable.

In the case of cryolite *Roth* and *Bertram* [1] found from the calorimetric measurements $\Delta H_f(\text{Na}_3\text{AlF}_6) = 16.64 \text{ kcal mol}^{-1} = 69.62 \text{ kJ mol}^{-1}$. *Kelley* [2] reported for this quantity the value $20.85 \text{ kcal mol}^{-1} = 87.24 \text{ kJ mol}^{-1}$. The latter value has been recommended also in the tables published in 1952 [3].

Later *O'Brien* and *Kelley* [4] obtained for $\Delta H_f(\text{Na}_3\text{AlF}_6)$ the value of $27.640 \text{ kcal mol}^{-1} = 115.65 \text{ kJ mol}^{-1}$. However, it should be pointed out that these authors reported the temperature of fusion of cryolite 1300 K, which is about 14–21 K higher than the values found by other authors. The literature data on calorimetrically determined values of the molar enthalpy of fusion of cryolite are summarized in Table 1. It can be seen that the values are scattered in the range

Table 1

Temperatures of fusion $T_f(\text{Na}_3\text{AlF}_6)$ and calorimetrically obtained values of the molar enthalpy of fusion of cryolite $\Delta H_f(\text{Na}_3\text{AlF}_6)$

Authors	Ref.	Year	$T_f(\text{Na}_3\text{AlF}_6)$ K	$H_f(\text{Na}_3\text{AlF}_6)$ kJ mol ⁻¹
<i>Roth and Bertram</i>	[1]	1929	1000	69.62
<i>Kelley</i>	[2]	1949		87.24
<i>O'Brien and Kelley</i>	[4]	1957	1300	115.65
<i>Brynestad et al.</i>	[5]	1960	1282	115.39
<i>Frank</i>	[6]	1961	1279	111.75
<i>Rolin and Bernard</i>	[7]	1962	1282	111.29
<i>Rolin and Rey</i>	[8]	1966	1282	112.97
<i>Holm</i>	[9]	1971	1284	115.06
JANAF	[10]	1971	1285	107.28
<i>Holm and Grönvold</i>	[11]	1973	1284	113.39
Mean value				105.96

69.6–115.7 kJ mol⁻¹. Arithmetic mean of these values is 106 kJ mol⁻¹, the maximum positive deviation from the mean is 8.4 % and the minimum negative deviation even 34.3 %. These differences suggest that it can be useful to determine the value of $\Delta H_f(\text{Na}_3\text{AlF}_6)$ by another independent method. High-temperature cryometry seems to be suitable for this purpose because it can give without greater experimental difficulties the results having uncertainty lower than ± 5 % [12]. In comparison with the calorimetric method the high-temperature cryometry is considerably less expensive and the results can be obtained in a relatively short time.

The cryometric determination of the enthalpy of fusion of substance *i* is based on measurement of the slope of the tangent to the liquidus curve of the component *i* in a binary or pseudobinary eutectic system *i*—*j*. The method can be used only if in the studied system no solid solution on the basis of the substance *i* is formed. It has been proved [13] that if the component *i* is a complex compound which thermally dissociates under melting then for the slope of the tangent $k^0(\text{R})$ in a eutectic system Z—R it holds

$$k^0(Z) = \lim_{x(R) \rightarrow 0} \frac{\Delta T(Z)}{\Delta x(R)} = \frac{R \cdot T_f^2(Z)}{\Delta H_f(Z)} \frac{1}{a_0(Z)} \lim_{x(Z) \rightarrow 1} \frac{da(Z)}{dx(Z)} \quad (1)$$

where

$\Delta T(Z)$ is the decrease of the liquidus temperature of the compound Z caused by the presence of the substance R in the binary system Z—R,

$\Delta x(R)$ is the concentration of substance R (given in mole fractions) in the solid mixture Z + R,

$T_f(Z)$ is the experimentally determined temperature of fusion of the pure solid compound Z,

$a_0(Z)$ is the activity of the compound Z. It is equal to the mole fraction of the thermally nondissociated compound Z in solution which results at melting of the pure solid compound Z. It follows that $a_0(Z) < 1$. As a standard state we choose the melt which results from melting of pure complex compound. We postulate that the activity coefficients of all substances which are present in this melt equal to one. Therefore their activities equal their mole fractions.

$a(Z)$ is the activity of the compound Z in the melt with substance R,

$x(Z)$ is the mole fraction of the compound Z in the solid mixture Z + R. It holds $x(Z) + x(R) = 1$.

For Stortenbeker's correction factor $k^{st}(R/Z)$ which equals in this case the number of new species which are formed in the melt of pure solid compound Z as a consequence of the addition of one molecule of the substance R it holds [13]

$$k^{st}(R/Z) = \frac{1}{a_0(Z)} \lim_{x(Z) \rightarrow 1} \frac{da(Z)}{dx(Z)} \quad (2)$$

Pure solid cryolite partly thermally dissociates under melting according to the scheme $\text{Na}_3\text{AlF}_6 \rightleftharpoons 2\text{NaF} + \text{NaAlF}_4$ [14]. Therefore in the mixture which is formed by melting of 1 mole of solid cryolite there coexist $(1 - b_0)$ moles of Na_3AlF_6 , $2b_0$ moles of NaF, and b_0 moles of NaAlF_4 . b_0 denotes the degree of thermal dissociation of pure compound Z at its melting point. $0 < b_0 < 1$. For true mole fractions of components of the melt which is formed by melting of solid cryolite it holds

$$y_0(\text{Na}_3\text{AlF}_6) = \frac{1 - b_0}{1 + 2b_0} \quad (3)$$

$$y_0(\text{NaF}) = \frac{2b_0}{1 + 2b_0} \quad (4)$$

$$y_0(\text{NaAlF}_4) = \frac{b_0}{1 + 2b_0} \quad (5)$$

For the equilibrium constant of thermal dissociation of pure molten cryolite it holds

$$K^0(\text{Na}_3\text{AlF}_6, \text{dis}) = \frac{a^2(\text{NaF}) \cdot a(\text{NaAlF}_4)}{a(\text{Na}_3\text{AlF}_6)} \quad (6)$$

As a consequence of the chosen standard state it holds for all species of the melt formed by melting of pure solid cryolite that their activities are equal to their mole fractions. Therefore we can substitute in eqn (6) activities by mole fractions of the corresponding substances, which results (after rearrangement) in

$$K^0(\text{Na}_3\text{AlF}_6, \text{dis}) = \frac{4b_0^3}{(1-b_0) \cdot (1+2b_0)^2} \quad (7)$$

Let us consider a mixture consisting of x moles of pure solid cryolite and $(1-x)$ moles of substance R. Let us assume for simplicity that substance R is an ionic compound which electrolytically dissociates into cation Na^+ (which is common with cations resulting from electrolytical dissociation of cryolite) and anion A^- which is new (noncommon) with respect to cryolite. In molten mixture there coexist now $x(1-b)$ moles Na_3AlF_6 , $2xb$ moles NaF , xb moles NaAlF_4 , and $(1-x)$ mole NaA . b denotes the degree of thermal dissociation of cryolite in the melt containing also substance NaA . $0 < b < 1$, $b_0 \neq b$. For true mole fractions of substances in the molten mixture $\text{Na}_3\text{AlF}_6 + \text{NaA}$ it holds

$$y(\text{Na}_3\text{AlF}_6) = \frac{x(1-b)}{1+2xb} \quad (8)$$

$$y(\text{NaF}) = \frac{2xb}{1+2xb} \quad (9)$$

$$y(\text{NaAlF}_4) = \frac{xb}{1+2xb} \quad (10)$$

$$y(\text{NaA}) = \frac{1-x}{1+2xb} \quad (11)$$

If we assume an ideal thermodynamic behaviour of substances (which holds satisfactorily for mole fractions $y(i)$ that are close to the values $y_0(i)$ in eqns (3–5) we obtain for the equilibrium constant of thermal dissociation of cryolite in its molten mixture with NaA the relationship

$$K(\text{Na}_3\text{AlF}_6, \text{dis}) = \frac{4x^2b^3}{(1-b) \cdot (1+2xb)^2} \quad (12)$$

If the temperature interval is not too broad — which is for the cryometric method always fulfilled — we can write the following equality

$$K^0(\text{Na}_3\text{AlF}_6, \text{dis}) = K(\text{Na}_3\text{AlF}_6, \text{dis}) \quad (13)$$

Let us consider the case when the substance NaA brings into the melt only one new particle, viz. the anion A^- . It holds $k^{St}(NaA/Na_3AlF_6) = 1$. Then for the proof of thermodynamic correctness of cryometry performed on the basis of cryolite it is sufficient to show that the same result can be derived from eqn (2) for $Z = Na_3AlF_6$ and $R = NaA$.

Gilbert *et al.* [15] have used for determination of the degree of dissociation of cryolite Raman spectroscopy. They found $b_0 = 0.25$. If we introduce this value into eqn (7) we find $K^0(Na_3AlF_6, dis) = 0.037037$. For x close to one (e.g. 0.95, 0.96, ... 0.99) we can calculate according to eqn (13) for each value of x the corresponding value of b and introduce the resulting pairs (x, b) into eqn (8). Then knowing $x(Na_3AlF_6)$ we can calculate according to eqn (2) the value $k^{St}(R/Z)$ and compare it with the value of $k^{St}(R/Z) = 1$ resulting from the experimental experience. Calculation of the quantity $k^{St}(R/Z)$ according to eqn (2) is a time-consuming procedure. Therefore it can be recommended to calculate the series of values

$$\frac{1}{a(Z)} \frac{\Delta a(Z)}{\Delta x(Z)} = k^{St}(NaA/Na_3AlF_6) \quad (14)$$

($Z = Na_3AlF_6$) as a function of x and extrapolate it to $x \rightarrow 1$. Results of this calculation are summarized in Table 2. It follows from these data that for $x(Z) \rightarrow 1$, $k^{St}(NaA/Z) \rightarrow 1$, which is the condition which must be fulfilled when the substance NaA brings into pure molten cryolite just one new particle.

In this work as substance $NaA = R$ also a complex compound (viz. Na_3FSO_4) was used. The degree of thermal dissociation of this substance is considerably higher than that of cryolite [16]. Therefore it is necessary to prove that Na_3FSO_4 really "brings" into molten cryolite only one new particle.

Let us assume that the degree of thermal dissociation of Na_3FSO_4 when it is infinitely diluted in cryolite equals d_∞ . Then from one molecule of Na_3FSO_4 we

Table 2

Stortenbeker's correction factor $k^{St}(Na_3FSO_4/Na_3AlF_6)$ for the liquidus of cryolite in the system $Na_3AlF_6-Na_3FSO_4$ as a function of mole fraction of cryolite, $x(Na_3AlF_6)$, the degree of thermal dissociation b of cryolite in the melt, and activity of cryolite $a(Na_3AlF_6)$ in the same melt

$x(Na_3AlF_6)$	b	$a(Na_3AlF_6)$	$k^{St}(Na_3FSO_4/Na_3AlF_6)$
0.95	0.25649	0.47490	1.05151
0.96	0.25516	0.47992	1.04263
0.97	0.25384	0.48495	1.03187
0.98	0.25254	0.48998	1.01729
0.99	0.25126	0.49499	1.00705
1.00	0.25000	0.50000	(1.00100)

obtain 3Na^+ , $(1 - d_\infty)\text{FSO}_4^{3-}$, $d_\infty\text{F}^-$, and $d_\infty\text{SO}_4^{2-}$ ions. With respect to molten cryolite only the particles FSO_4^{3-} and SO_4^{2-} can be regarded as new (noncommon) particles. Their total sum equals $(1 - d_\infty) + d_\infty = 1$, regardless of the value of d_∞ . Thus in agreement with our assumption we finally obtain $k^{\text{St}}(\text{R/Z}) = k^{\text{St}}(\text{Na}_3\text{FSO}_4 / \text{Na}_3\text{AlF}_6) = 1$.

Experimental

The liquidus curve was obtained by a classical thermal analytical method [17]. The measurement was carried out in open atmosphere. Both cooling and heating curves were recorded. All used chemicals were of anal. grade (Lachema, Brno). Aluminium fluoride was further purified by sublimation at about 1550 K in a platinum apparatus. Samples were melted in a laboratory resistance furnace. Temperature was measured by means of a PtRh10—Pt thermocouple (diameter of wires 0.5 mm). Cool junction of the thermocouple was kept at 273.2 K. (A mixture of water and crushed ice in Dewar flask was used to maintain this temperature.) The hot junction of the thermocouple was immersed directly in the melt. The thermocouple was calibrated on melting points of NaF, Na_2SO_4 , NaCl, KCl, and a eutectic mixture NaCl + Na_2SO_4 (Table 3). EMF of the thermocouple was recorded on an automatic compensation recorder of the type MKET. The samples (about 30 g) were melted in platinum crucibles. The rate of cooling or heating was 0.5—1.0 K min^{-1} .

Complex compounds Na_3AlF_6 and Na_3FSO_4 were prepared from NaF + AlF_3 and NaF + Na_2SO_4 , respectively.

For cryometric determination of $\Delta H_f(\text{Na}_3\text{AlF}_6)$ temperature of liquidus of six mixtures of Na_3AlF_6 with Na_3FSO_4 was investigated. Concentration of Na_3FSO_4 ranged in the interval 0—5 mole %. All measurements were carried out at strictly constant conditions. Special attention was paid to overheating of the melt which never exceeded liquidus temperature of the corresponding mixture more than 10—15 K. Each determination of the liquidus temperature was twice repeated and for cryometric calculation of enthalpy of fusion the data with lowest scattering were used. Experimental values of the temperature of liquidus of investigated mixtures are summarized in Table 4.

Table 3
Substances used for calibration of PtRh10—Pt thermocouple

Substance	Type of phase transition	Temperature of phase transition °C	Ref.
NaF	Melting	1266.7	[23]
Na_2SO_4	Melting	1158.0	[18]
NaCl	Melting	1074.0	[10]
KCl	Melting	1044.0	[10]
NaCl + Na_2SO_4	Eutectic crystallization	901.0	[19]

These data cannot give a definitive answer on problem of formation of solid solutions on the basis of Na_3AlF_6 . However, if the solid solution does exist interval of its existence must be so narrow that it cannot influence the application of the cryometric method for determination of the molar enthalpy of melting of cryolite.

Table 4

Experimentally determined liquidus temperature of Na_3AlF_6 , the values of $\Delta T(\text{Na}_3\text{AlF}_6)$, and the ratio $\Delta T(\text{Na}_3\text{AlF}_6)/x(\text{Na}_3\text{FSO}_4)$ in the system $\text{Na}_3\text{AlF}_6\text{—Na}_3\text{FSO}_4$

$x(\text{Na}_3\text{FSO}_4)$	$T(\text{Na}_3\text{AlF}_6)$ K	$\Delta T(\text{Na}_3\text{AlF}_6)$ K	$\Delta T(\text{Na}_3\text{AlF}_6)/x(\text{Na}_3\text{FSO}_4)$
0.00	1282.7	—	—
0.01	1281.5	1.2	120
0.02	1280.0	2.7	135
0.03	1278.6	4.1	137
0.04	1276.8	5.9	148
0.05	1275.5	7.2	144

Results and discussion

The experimental results were treated by the least-squares method [20]. It was found that the dependence $\Delta T(Z)/x(R) = f[x(R)]$ can be approximated by a straight line. Its equation was found to be

$$\Delta T(Z)/x(R) = 118.5 + 610x(R) \quad (15)$$

Residual sum of squares of deviations S_0 equals 90.7 and the statistical estimation of the standard deviation is 5.5. Statistical estimation of the standard deviation of the first term on the right-hand side of eqn (15) is $s_a = 5.77$, i.e. 4.9 %. Thus $k^0(\text{Na}_3\text{AlF}_6) = 118.5$ and for the molar enthalpy of fusion of cryolite it holds

$$\Delta H_f(\text{Na}_3\text{AlF}_6) = \frac{R \cdot T_f^2(\text{Na}_3\text{AlF}_6)}{k^0(\text{Na}_3\text{AlF}_6)} k^{\text{st}}(\text{Na}_3\text{FSO}_4/\text{Na}_3\text{AlF}_6) \quad (16)$$

As we have above proved $k^{\text{st}}(\text{Na}_3\text{FSO}_4/\text{Na}_3\text{AlF}_6) = 1$. Then it follows from eqn (16) that $\Delta H_f(\text{Na}_3\text{AlF}_6) = 115.44 \text{ kJ mol}^{-1}$, uncertainty of this estimation being $\pm 4.9 \%$. According to the monograph [21] the most probable value of the quantity $\Delta H_f(\text{Na}_3\text{AlF}_6)$ is $(114 \pm 2) \text{ kJ mol}^{-1}$, which is in very good agreement with the result obtained in this work. It follows that the enthalpy of fusion presented by Roth and Bertram [1] ($\Delta H_f(\text{Na}_3\text{AlF}_6) = 69.6 \text{ kJ mol}^{-1}$) is too low. If we take the value 114 kJ mol^{-1} as 100 % the negative deviation of the data reported in [1] is about 40 %. Such a great deviation cannot be explained by an unsuitable

experimental technique. Using the same apparatus the quoted authors [1] found for sodium chloride $\Delta H_f(\text{NaCl}) = 7.41 \text{ kcal mol}^{-1} = 31.0 \text{ kJ mol}^{-1}$ which is close to the value found by Kelley [22] viz. $6.85 \text{ kcal mol}^{-1} = 28.66 \text{ kJ mol}^{-1}$. It is seen that in this case the data by Roth and Bertram differ only about 8.2 %, which is acceptable with regard to the experimental technique available in the year 1930. Therefore we may reasonably assume that in the case of cryolite an experimental error influenced the results published in [1].

In conclusion we can state that determination of the enthalpy of fusion from the cryometric data can be a useful supplement to the results obtained by calorimetry. It can be especially recommended for checking a principal correctness of the results obtained by other methods.

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