Ionic Species in Cryolite–Sodium Pyrophosphate Melts

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Various models for possible ionic species present in the molten system cryolite–sodium pyrophosphate are discussed on the basis of previous phase diagram data. Earlier work has suggested that cryolite may be dissociated completely into Al^{3+} and F^- ions for small additions of cryolite in molten sodium pyrophosphate. However, this is considered highly unlikely, and the experimental data may rather be interpreted by the occurrence of the reaction:

$$2P_2O_7^{4-} + AlF_6^{3-} = 2PO_4^{3-} + 2PO_3F^{2-} + AlF_4^-.$$

Dimerization of PO_3F^{2-} to $P_2O_6F_2^{4-}$ ions may be possible. On the cryolite side of the system, Al–O–F complexes may also be formed.

The system cryolite–sodium pyrophosphate has been studied previously by del Campo.[1] The phase diagram was determined by differential thermal analysis, and the results are shown in Fig. 1. This was found to be a simple eutectic system, with the eutectic point at 1021 K and 66.7 mole % $Na_4P_2O_7$. No solid solution was observed.

On the basis of the measured liquidus temperatures at the sodium pyrophosphate end of the phase diagram, del Campo[1] examined various dissociation schemes for the dissolution of cryolite in the melt:

Model I. Simple ionic dissociation:

$$Na_3AlF_6 \rightarrow 3Na^+ + AlF_6^{3-}. \tag{1}$$

Model II. Complete dissociation of the anion in cryolite to an Al–F species:

$$Na_3AlF_6 \rightarrow 3Na^+ + AlF_4^- + 2F^-. \tag{2}$$

Fig. 1. The phase diagram for the system $Na_3AlF_6-Na_4P_2O_7$ according to del Campo.[1]

Model III. Complete dissociation of the anion in cryolite to monoatomic aluminium ions:

$$Na_3AlF_6 \rightarrow 3Na^+ + Al^{3+} + 6F^-. \tag{3}$$

In all three cases it was assumed that sodium pyrophosphate was completely dissociated according to the equation:

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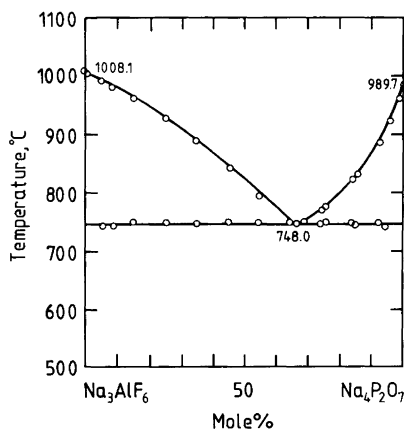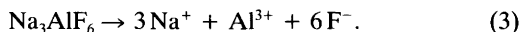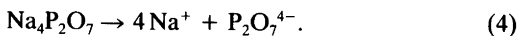
$$Na_4P_2O_7 \rightarrow 4\,Na^+ + P_2O_7^{4-}. \qquad (4)$$

Furthermore, the assumption of ideal ionic mixing was made. As seen from Fig. 2, the best agreement with the experimental data[1] was obtained for model III. This implies that seven "new" species are formed when small amounts of cryolite are dissolved in molten sodium pyrophosphate.
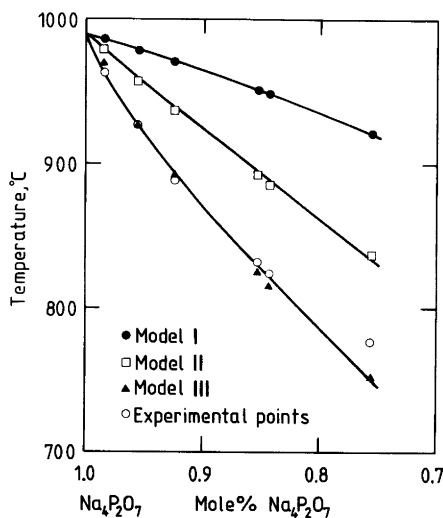

Fig. 2. Freezing point depression of $Na_4P_2O_7$ with addition of Na_3AlF_6 according to calculations by del Campo.[1] Models I, II and III are described in the text.

This conclusion, however, is considered highly unlikely. It is generally accepted in the literature[2] that the small, trivalent aluminium ion does not exist as a free ion in cryolite melts, but is bound to fluoride ions in the form of complex species such as AlF_4^- and AlF_6^{3-}. Thus, it is the purpose of the present paper to use the previous experimental data[1] to arrive at a more realistic and probable model for the dissolution of cryolite in molten sodium pyrophosphate. However, as always when fitting theoretical models to experimental data, even if the model fit is very good one should be cautious in interpreting the results.

Theory

From simple thermodynamics the following equation may be derived:

$$-\log x_{Na_4P_2O_7} = \frac{\Delta H_m^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right). \qquad (5)$$

Here, $x_{Na_4P_2O_7}$ is the mole fraction of sodium pyrophosphate in the melt, ΔH_m° is the molar heat of melting of this compound and T_o is its absolute melting temperature ($=1263$ K); T is an arbitrary absolute temperature and R is the universal gas constant. Pure molten $Na_4P_2O_7$ is then chosen as the standard state and an ideal system $Na_4P_2O_7$ – Na_3AlF_6 is assumed.

In eqn. (5) the mole fraction $x_{Na_4P_2O_7}$ may be replaced by:

$$x_{Na_4P_2O_7} = x^4_{Na^+} \cdot x_{P_2O_7^{4-}}, \qquad (6)$$

where x_{Na^+} is the cationic mole fraction of Na^+ ions in the melt (equal to unity in the present case) and $x_{P_2O_7^{4-}}$ is the anionic mole fraction of the $P_2O_7^{4-}$ ions. If we then combine eqns. (5) and (6), and plot $-\log(x^4_{Na^+} \cdot x_{P_2O_7^{4-}})$ versus $(1/T - 1/T_o)$, the slope of the curve should be proportional to the molar heat of melting, ΔH_m°, of sodium pyrophosphate.

Results

ΔH_m° of $Na_4P_2O_7$. The heat of melting of sodium pyrophosphate has been determined by Wei,[3] using an inverse drop calorimeter. The value obtained was 50.4 ± 2.0 kJ mol^{-1} at the melting point, 1263 K. This agrees very well with the value of 50.2 ± 1.3 kJ mol^{-1} reported by Gorbovskaya and Viting.[4]

A new model (IV). As before, we will assume that cryolite dissociates completely according to model II:

$$Na_3AlF_6 \rightarrow 3\,Na^+ + AlF_4^- + 2\,F^-. \qquad (2)$$

The new model (model IV) includes the additional assumption that the pyrophosphate ions react with the fluoride ions according to the equation:

$$P_2O_7^{4-} + F^- = PO_4^{3-} + PO_3F^{2-}. \qquad (7)$$
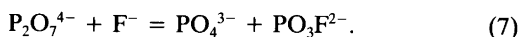
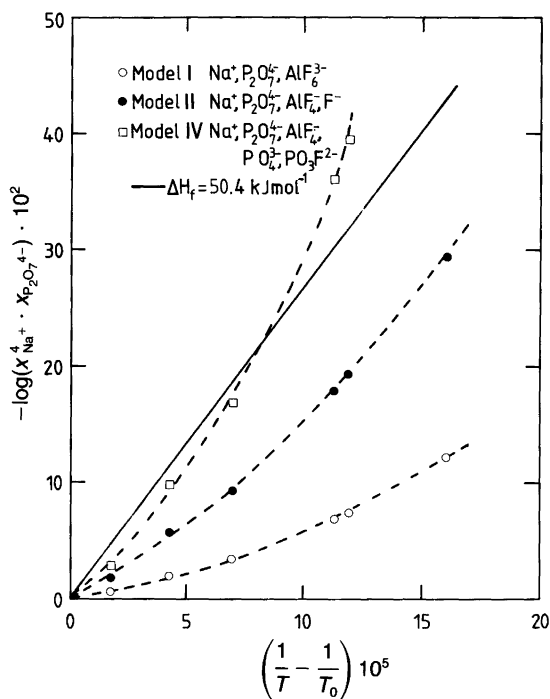As a first approximation, it will be assumed that reaction (7) will shift reaction (2) completely to

Fig. 3. Various models for the dissolution of Na_3AlF_6 in molten $Na_4P_2O_7$. The straight line corresponds to the experimental heat of melting of $Na_4P_2O_7$ determined by Wei.[3] The models are described in the text.

the right, and thus all of the AlF_6^{3-} ions will be dissociated to AlF_4^- and F^- ions.

Model comparison. Models I, II and IV are compared in Fig. 3, which shows $-\log(x^4_{Na^+} \cdot x_{P_2O_7^{4-}})$ versus $(1/T - 1/T_0)$. Models I and II give curves with slopes that are much smaller than that of the line corresponding to the measured heat of melting of sodium pyrophosphate. Model IV, in contrast, gives reasonably good agreement for abscissa values up to nine units of $(1/T - 1/T_0) \cdot 10^5$. This corresponds to a mole fraction of $Na_4P_2O_7$ of 0.87 and a mole fraction of Na_3AlF_6 of 0.13. Thus, within the pyrophosphate-rich portion of the system model IV gives much better agreement with the experimental data than models I and II.

According to model IV, the net ionic equation for the dissolution of cryolite in molten sodium pyrophosphate may be written as:

$$2 P_2O_7^{4-} + AlF_6^{3-} = AlF_4^- + 2 PO_4^{3-}$$
$$+ 2 PO_3F^{2-}. \tag{8}$$
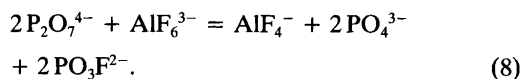
This reaction gives 5 "new" species in the melt for each mole of cryolite added.

The model may be refined further by assuming that the AlF_6^{3-} ions do not react completely, and thus the equilibrium reaction:

$$AlF_6^{3-} \rightleftharpoons AlF_4^- + 2 F^- \tag{9}$$
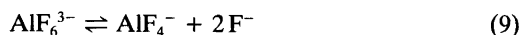
is then not *completely* shifted to the right. This means that small amounts of AlF_6^{3-} and F^- ions may be present in the melt together with AlF_4^-, $P_2O_7^{4-}$, PO_4^{3-} and PO_3F^{2-} ions.

Discussion

Pyrophosphate-rich melts. Julsrud[5] has reported calorimetric data for the high-temperature heats of mixing for the sodium fluoride–sodium pyrophosphate system. The results were interpreted in terms of structural species formed in the molten mixture. He suggested that pure molten sodium pyrophosphate may be expected to be dissociated to some degree according to the equation:

$$2 P_2O_7^{4-} \rightleftharpoons PO_4^{3-} + P_3O_{10}^{5-}. \tag{10}$$
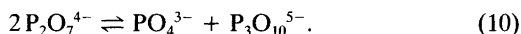
When small amounts of sodium fluoride are added an additional equilibrium reaction may be established:

$$2 P_2O_7^{4-} + 2 F^- \rightleftharpoons 2 PO_4^{3-} + P_2O_6F_2^{4-}. \tag{11}$$
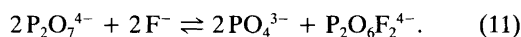
The orthophosphate ions formed according to eqn. (11) will reduce the activity of the pyrophosphate ions and thus shift the equilibrium of eqn. (10) somewhat to the left.

The most interesting proposal by Julsrud[5] is therefore reaction (11), which implies the formation of the dimer of PO_3F^{2-}, namely $P_2O_6F_2^{4-}$. Apart from that, reactions (7) and (11) are identical. Whether this ion exists as a monomeric or a dimeric species in these melts is difficult to determine, but the agreement with the data in Fig. 3 is poorer when the dimer is introduced in model IV.

Thus, the main function of cryolite when dissolved in molten sodium pyrophosphate appears

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to be to supply fluoride ions to the reaction with the pyrophosphate ions according to eqn. (7).

Cryolite-rich melts. These mixtures were also studied by del Campo.[1] He found that model IV gave a better agreement with the liquidus data in the phase diagram than model II, although some deviation was apparent. Here, we assume that the following reaction takes place between the AlF_6^{3-} ion and the pyrophosphate ion:

$$2 AlF_6^{3-} + P_2O_7^{4-} = Al_2OF_8^{4-} + 2 PO_4^{2-}$$
$$+ 2 F^-. \tag{12}$$
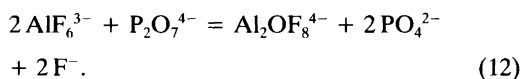
Thus, the effect of the pyrophosphate ions will be mainly to provide oxide ions to form aluminium–oxygen–fluorine anions. The species $Al_2OF_8^{4-}$ has been shown to be the dominant complex ion in cryolite melts with small additions of alumina.[6]

References

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