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Estimated Heats of Fusion of Fluoride Salt Mixtures Suitable for Thermal Energy Storage Applications

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ESTIMATED HEATS OF FUSION OF FLUORIDE SALT MIXTURES SUITABLE

FOR THERMAL ENERGY STORAGE APPLICATIONS

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SUMMARY

The heats of fusion of several fluoride salt mixtures with melting points greater than 973 K have been estimated from a coupled analysis of the available thermodynamic data and phase diagrams. Simple binary eutectic systems with and without terminal solid solutions, binary eutectics with congruent melting intermediate phases, and ternary eutectic systems were considered. Several combinations of salts have been identified, most notably the eutectics $\text{LiF}-22\text{CaF}_2$ and $\text{NaF}-60\text{MgF}_2$ which melt at 1039 and 1273 K respectively which possess relatively high heats of fusion/gm (>0.7 kJ/g). Such systems would seemingly be ideal candidates for the light weight, high energy storage media required by the thermal energy storage unit in advanced solar dynamic power systems envisioned for the future space missions.

INTRODUCTION

Thermal energy storage (TES) subsystems will be required for advanced solar dynamic power systems to provide electric power for future space missions during periods of low or nonexistent solar insolation. While batteries or fuel cells can supply the necessary energy, they impose a large weight penalty. Less heavy alternatives have been suggested, and these generally involve the use of a material to store heat for an engine turning a generator. For example, solar radiation can be utilized to melt a solid while the solar dynamic power system is in sun light, and then this energy can be extracted from the solidifying melt when the power system is in eclipse (refs. 1 and 2).

One of the prime criteria for selection of a solid to liquid phase change TES material is a high heat of fusion. Fluoride salts of Na, Li, Mg, K, and Ca have the highest enthalpies of fusion among all the molten salts; however they can only be used if the operating temperature of the heat engine is compatible with their melting points. This limitation can be removed if eutectic mixtures of two or more fluoride salts are considered. Unfortunately, data are lacking on the heats of fusion for most eutectics; therefore, as a first point for the selection of potential salt systems, the heats of fusion must be estimated.

This report describes the estimation of latent heat of fusion of several multicomponent fluoride eutectics as determined by a coupled analysis of the

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available thermodynamic data and the phase diagrams. All systems chosen have melting points above 973 K to be consistent with the potential operating temperatures of Brayton and Sterling cycle engines proposed for the advanced solar dynamic power systems.

SYMBOL LIST

| | |
|-----------------------------------|---|
| A', B', C' | constants in the expression (eqs. (4), (5), and (7)) |
| a_i | activity of compound i in the solution |
| $C_{p,i}^S$ | heat capacity of a solid compound i , $\text{JK}^{-1} \text{mol}^{-1}$ |
| $C_{p,i}^L$ | heat capacity of a compound i in the liquid state, $\text{JK}^{-1} \text{mol}^{-1}$ |
| e | eutectic |
| G_i^E | excess partial molar Gibb's free energy for compound i in the solution, kJ/mol |
| q_i | charge of the cation |
| S_M^E | excess entropy of mixing in the solution, $\text{JK}^{-1} \text{mol}^{-1}$ |
| s | solid |
| T | dry temperature, K |
| T_M | melting point, K |
| X_i | mole fraction of a compound i in a solution |
| X_i^i | equivalent ionic fraction of a compound i in a solution |
| X_i^α | mole fraction of compound i in the α solid solution that is in equilibrium with the eutectic |
| X_i^β | mole fraction of compound i in the β solid solution that is in equilibrium with the eutectic |
| γ_i | activity coefficient of compound i in the solution |
| γ_i^e | activity coefficient of compound i in the eutectic melt |
| $\gamma_i^\alpha, \gamma_i^\beta$ | activity coefficient of compound i in the α and β solid solution, respectively |
| $\Delta G_{f,i}^0(T)$ | Gibb's free energy of fusion of a compound i at any temperature other than the melting point, kJ/mol |

| | |
|--|--|
| ΔH_{ef} | heat of fusion of the eutectic, kJ/mol |
| ΔH_{eM} | heat of mixing in the melt at the eutectic, kJ/mol |
| $\Delta H_{em}^{A-B}, \Delta H_{em}^{A-B-C}$ | heat of mixing in the binary A-B and ternary A-B-C melt at the eutectic composition, kJ/mol |
| $\Delta H_{f,i}^T$ | heat of fusion of a compound i at the melting point, kJ/mol |
| ΔH_i | partial molar enthalpy of mixing for the compound i in the solution, kJ/mol |
| $\Delta H_{f,i}^T$ | heat of fusion of a compound i at any temperature other than the melting point, kJ/mol |
| ΔH_M | heat of mixing in a mole of solution, kJ/mol |
| ΔH_M^i | heat of mixing per equivalent of solution, kJ/equivalent. |
| ΔH_M^α | heat of mixing in the α solid solution, kJ/mol |
| ΔH_M^β | heat of mixing in the β solid solution, kJ/mol |
| ΔH_ϵ^f | heat of formation of the intermediate phase ϵ in the binary system A-B from pure compounds A and B, kJ/mol |
| ΔS_{ef} | entropy of fusion of the eutectic, JK ⁻¹ mol ⁻¹ |
| $\Delta S_{eM}^{id(l)}$ | ideal entropy of mixing for the eutectic liquid, JK ⁻¹ mol ⁻¹ |
| $\Delta S_{f,i}$ | entropy of fusion of compound i , JK ⁻¹ mol ⁻¹ |
| ΔS_M | total entropy of mixing, JK ⁻¹ mol ⁻¹ |
| ΔS_M^{id} | ideal entropy of mixing in a solution, JK ⁻¹ mol ⁻¹ |
| $\Delta S_{\alpha M}^{id}$ | ideal entropy of mixing for α solid solution that is in equilibrium with the eutectic, JK ⁻¹ mol ⁻¹ |
| $\Delta S_{\beta M}^{id}$ | ideal entropy of mixing for β solid solution that is in equilibrium with the eutectic, JK ⁻¹ mol ⁻¹ |
| ϵ | intermediate compound |
| l | liquid |

THERMODYNAMIC CONSIDERATIONS

General Approach

The heat of fusion of any eutectic, ΔH_{ef} , can be directly calculated via

$$\begin{array}{l} \text{Heat of} \\ \text{fusion of} \\ \text{the eutectic} \end{array} = \begin{array}{l} \text{Heat of fusion of} \\ \text{the individual} \\ \text{compounds at the} \\ \text{eutectic temperature} \end{array} + \begin{array}{l} \text{Heat of} \\ \text{mixing} \\ \text{in the} \\ \text{liquid} \end{array} - \begin{array}{l} \text{Heat of} \\ \text{mixing} \\ \text{in the} \\ \text{solid} \\ \text{solutions} \end{array} \quad (1)$$

or if the entropy of fusion, ΔS_{ef} , can be estimated for the eutectic, where

$$\begin{array}{l} \text{Entropy of} \\ \text{fusion of} \\ \text{the eutectic} \end{array} = \begin{array}{l} \text{Entropy of} \\ \text{fusion of} \\ \text{the individual} \\ \text{compounds} \end{array} + \begin{array}{l} \text{Entropy of} \\ \text{mixing in} \\ \text{the liquid} \end{array} - \begin{array}{l} \text{Entropy of} \\ \text{mixing of} \\ \text{the solid} \\ \text{solutions} \end{array} \quad (2)$$

and

$$\Delta H_{ef} = \Delta S_{ef} \times T_e \quad (2a)$$

where T_e is the eutectic temperature. Unfortunately, most of the terms on the right hand side of these equations have not been experimentally measured; hence they must be estimated through standard thermodynamic models and expressions. In this study ΔH_{ef} is computed by both equations (1) and (2a), and a comparison made; close agreement of the two values would indicate a reliable estimate.

Calculation of Terms for Equations (1) and (2)

Heats of fusion of pure materials are only known at their melting points, but they can also be calculated for other temperatures T from

$$\Delta H_{f,i}^T = \Delta H_{f,i}^{T_M} + \int_{T_M}^T (C_{p,i}^L - C_{p,i}^S) dT \quad (3)$$

where $\Delta H_{f,i}^T$ and $\Delta H_{f,i}^{T_M}$ are the heats of fusion of component i at temperature T and the melting point T_m respectively; and $C_{p,i}^L$ and $C_{p,i}^S$ are the heat capacities of the liquid and solid phases. While $C_{p,i}^L$ generally varies little with temperature, $C_{p,i}^S$ is a strong function of temperature

(ref. 3)

$$C_{p,i}^S = A' + B' \cdot 10^{-3}T + C' \cdot 10^5 T^{-2} \quad (4)$$

where A' , B' , and C' are constants available from standard tables (ref. 4).

The heat of mixing ΔH_M of many binary fluoride melts have been determined by Kleppa and co-workers (refs. 5 to 8) and fitted to a polynomial expression of the type

$$\Delta H_M = X_A X_B (A' + B' X_B + C' X_B^2 + D' X_B^3) \quad (5)$$

where X_A and X_B are the mole fractions of substances A and B, respectively in the mixture and A' , B' , C' , and D' are the constants.

The entropy of mixing ΔS_M for a binary melt is the sum of the ideal entropy of mixing ΔS_M^{id} plus the excess entropy of mixing S_M^E where

$$\Delta S_M^{id} = -R [X_A \ln X_A + X_B \ln X_B] \quad (6)$$

and as suggested in reference 9

$$S_M^E = X_A X_B (A' + B' X_B + C' X_B^2 + D' X_B^3) \quad (7)$$

with R being the universal gas constant. In general the excess entropy of mixing in the melt will only be important if the enthalpy of mixing is large; otherwise S_M^E can be assumed to be zero.

Equations (5) to (7) can also be used to describe the thermodynamic properties of the solid solutions in which all the cations have the same valence. However, in charge asymmetric ionic solid solutions, the equivalent ionic fraction instead of the simple mole fraction is used to calculate the enthalpy and entropy of mixing (ref. 10). The equivalent ionic fraction X_i^i of a cation i is

$$X_i^i = \frac{q_i X_i}{\sum_j q_j X_j} \quad (8)$$

where q_i is the absolute charge of the cation i and the summation is conducted over all the cations in the solution. Substitution of the equivalent ionic fractions for A and B in equations (5) to (7) gives the enthalpy and entropy of mixing per equivalent of the binary solution.

When thermodynamic data for the solutions are not available, frequently estimates based on the phase diagrams (refs. 9 and 11) are made by first calculating the Gibbs free energy of fusion of a component at a given temperature along the liquidus and then relating this to the excess Gibbs energy of the component in solution via

$$RT \ln X_1^L + G_1^{E(L)} - RT \ln X_1^S - G_1^{E(S)} = -\Delta G_{f,1}^{O(T)} \quad (9)$$

where $G_1^{E(L)}$ is the excess partial molar Gibbs free energy for 1, $\Delta G_{f,1}^{O(T)}$ is the free energy of fusion 1 at the temperature corresponding to the liquidus point. ΔG_f^O can be determined from

$$\Delta G_{f,1}^{O(T)} = \Delta H_{f,1}^T - T \frac{\Delta H_{f,1}^{T_M}}{T_M} \quad (10)$$

The partial molar excess Gibbs free energy is given by

$$G_1^E = \Delta H_1 - TS_1^E \quad (11)$$

where ΔH_1 and S_1^E are the partial molar enthalpy of mixing and excess partial molar entropy of mixing, respectively, for component 1.

Each term in equation (11) can be related to simpler thermodynamic concepts via

$$a_1 = X_1 \cdot \gamma_1 \quad (12)$$

and

$$G_1^E = RT \ln \gamma_1 \quad (12a)$$

where a_1 and γ_1 are the activity and activity coefficient of 1, respectively; and for binaries the application of Gibbs-Duhem equation gives

$$\Delta H_1 = \Delta H_M + (1 - X_1) \frac{d\Delta H_M}{dX_1} \quad (13)$$

$$S_1^E = S_M^E + (1 - X_1) \frac{dS_M^E}{dX_1} \quad (14)$$

For ternary systems the heat of mixing can be estimated from the equation derived by Olson and Toop (ref. 12) which relates the ternary heat of mixing for a liquid solution consisting of A, B, and C, ΔH_M^{A-B-C} , as a function of the binary values of ΔH_M along composition paths with constant X_A/X_B , X_B/X_C , and X_A/X_C ratios:

$$\Delta H_M^{A-B-C} = (1 - X_C)^2 \left[\Delta H_M^{A-B} \right] X_A/X_B + (1 - X_A)^2 \left[\Delta H_M^{B-C} \right] X_B/X_C + (1 - X_B)^2 \left[\Delta H_M^{A-C} \right] X_A/X_C \quad (15)$$

where the meanings of the terms shown in equation (15) are graphically shown in figure 1.

APPLICATION OF THERMODYNAMIC PRINCIPLES TO THE ESTIMATION OF HEAT OF FUSION

In the following determinations the entropy of fusion of a component and the constants in the equations for enthalpies and entropies of mixing will be assumed to be temperature independent. For simplicity four categories of eutectics are considered: binary systems (1) with and (2) without terminal solid solutions or (3) with congruently melting intermediate compounds, and (4) ternary systems having no solid solutions.

Binary Eutectic Systems Without Terminal Solid Solutions

Heat of mixing known for the liquid. - The heat of fusion for the eutectic $AF_{q_A} - BF_{q_B}$ (ΔH_{ef}^{A-B}) can be directly calculated from the enthalpies of fusion for each salt at the eutectic temperature ($\Delta H_{f,A}^T, \Delta H_{f,B}^T$) and the heat of mixing of the liquid at the eutectic composition (ΔH_{eM}^L) via

$$\Delta H_{ef}^{A-B} = X_A^e \Delta H_{f,A}^T + X_B^e \Delta H_{f,B}^T + \Delta H_{eM}^L \quad (16)$$

Heat of fusion from entropy considerations. - The change in entropy during the melting of a eutectic can be expressed by

$$\Delta S_{ef}^{A-B} = X_A^e \Delta S_{f,A} + X_B^e \Delta S_{f,B} + \Delta S_{eM}^{id(l)} + S_{eM}^{E(l)} \quad (17)$$

Available heat of mixing data for the fluoride melt systems that do not exhibit an intermediate compound, indicate that only small deviations from ideality occur; hence the excess entropy of mixing will be assumed to be negligible. With ideal entropy of mixing calculated from equation (6), the heat of fusion follows directly from equation (2a).

Heat of mixing from phase diagram analysis. - Assuming excess entropy of mixing to be zero, the enthalpy of mixing of the salts at the eutectic can be calculated from the following equations:

$$-\Delta G_{f,A}^{o(T_e)} = RT \ln X_A^e + RT \ln \gamma_A^e \quad (18)$$

$$-\Delta G_{f,B}^{o(T_e)} = RT_e \ln (X_B^e \cdot \gamma_B^e) \quad (19)$$

$$\Delta H_{eM}^{AB} = X_A^e RT_e \ln \gamma_A^e + X_B^e RT_e \ln \gamma_B^e \quad (20)$$

where $\Delta G_{f,A}^{o(T_e)}$ and $\Delta G_{f,B}^{o(T_e)}$ are the Gibb's free energy of fusion of AF_{q_A} and BF_{q_B} , respectively at the eutectic temperature; γ_A^e and γ_B^e are the activity coefficient of AF_{q_A} and BF_{q_B} , respectively in the liquid at the eutectic composition. Substitution of ΔH_{eM}^{AB} in equation (16) gives the heat of fusion of the eutectic.

Example calculations. - Kleppa and co-workers have measured the heats of mixing for three systems (refs. 5 and 6) that exhibit a simple eutectic: KF-NaF, LiF-CaF₂ and NaF-CaF₂ where

$$\Delta H_M^{KF-NaF} = -334 X_{KF} \cdot X_{NaF} \text{ J/mol} \quad (21)$$

$$\Delta H_M^{LiF-CaF_2} = X_{LiF} \cdot X_{CaF_2} \left(-5271 - 376 X_{CaF_2} \right) \text{ J/mol} \quad (22)$$

$$\Delta H_M^{NaF-CaF_2} = X_{NaF} \cdot X_{CaF_2} \left(-19413 - 376 X_{CaF_2} \right) \text{ J/mol} \quad (23)$$

Estimated heats of fusion utilizing each of the above strategies for the simple binary eutectic systems are given in table II; the close agreement among the values is taken to signify a valid result.

Binary Eutectic Systems With Terminal Solid Solutions

Theory. - Birchenall and Riechman (ref. 13) have described a technique to estimate the enthalpy of fusion of the eutectic in binary systems with terminal solid solutions such as that shown in figure 2. At the eutectic temperature, where equilibrium is maintained among liquid of composition X_e and solid solutions of composition X_α and X_β , the heat of fusion per mole of eutectic is

$$\Delta H_{ef}^{AB} = (1 - X_e) \Delta H_{f,A}^{T_e} + X_e \Delta H_{f,B}^{T_e} + \Delta H_{eM}^{AB(l)} - \left(\frac{X_\beta - X_e}{X_\beta - X_\alpha} \right) \Delta H_{\alpha M}^{AB} - \left(\frac{X_e - X_\alpha}{X_\beta - X_\alpha} \right) \Delta H_{\beta M}^{AB} \quad (24)$$

where $\Delta H_{\alpha M}^{AB}$ is the heat of mixing of the α solid solution at composition X_α and $\Delta H_{\beta M}^{AB}$ is the heat of mixing of the β solid solution at composition X_β .

Similarly, assuming the excess entropy of mixing to be negligible, the entropy of fusion per mole of the eutectic can be written as

$$\Delta S_{ef}^{AB} = (1 - X_e) \Delta S_{f,A} + X_e \Delta S_{f,B} + \Delta S_{eM}^{id(l)} - \left(\frac{X_\beta - X_e}{X_\beta - X_\alpha} \right) \Delta S_{\alpha M}^{id} - \left(\frac{X_e - X_\alpha}{X_\beta - X_\alpha} \right) \Delta S_{\beta M}^{id} \quad (25)$$

where $\Delta S_{\alpha M}^{id}$ is the ideal entropy of mixing of the α solid solution at composition X_α , and $\Delta S_{\beta M}^{id}$ is the ideal entropy of mixing of the β solid solution at composition X_β .

LiF-MgF₂. - The LiF-MgF₂ phase diagram (fig. 2) demonstrates extensive solid solubility for both terminal solid solutions; however the exact limits are not clear at the eutectic temperature. For our calculations the following values were used: the LiF rich solid solution has 77 percent LiF,¹ and the MgF₂ rich solution has 61 percent LiF. The heat of mixing for the LiF-MgF₂ melt has been determined by Hong and Kleppa (ref. 8) at 1354 K, and it only showed a slight variation with composition:

$$\Delta H_M^{LiF-MgF_2} = X_{LiF} \cdot X_{MgF_2} \left(-24.09 - 2.36 X_{MgF_2} - 1.025 X_{MgF_2}^2 \right) \text{ kJ/mol} \quad (26)$$

No data exists as to the heat of mixing in the solid solutions; however they can be estimated by combination of phase diagram information with the heat of mixing data for the liquid and the Gibb's free energy of fusion of the components at the eutectic temperature. Assuming ideal entropies of mixing for both the solid and liquid solutions, equation (9) becomes

$$RT \ln X_i^l + RT \ln \gamma_i^l - RT \ln a_i^S = -\Delta G_{f,i}^{o(T_e)} \quad (27)$$

where the activity coefficients of LiF and MgF₂ in the melt can be derived from equations (11) to (13) and (26) as

$$RT \ln \gamma_{LiF}^l = -24091 X_{MgF_2}^2 - 2363 (1 - 2 X_{LiF}) X_{MgF_2}^2 - 1025 (1 - 3 X_{LiF}) X_{MgF_2}^2 \quad (28)$$

$$RT \ln \gamma_{MgF_2}^l = -24091 X_{MgF_2}^2 - 4727 X_{LiF}^2 \cdot X_{MgF_2} - 3075 X_{LiF}^2 \cdot X_{MgF_2}^2 \quad (29)$$

¹All compositions are given in mole percent.

Based on the equivalent ionic fraction approach the activities of LiF and MgF₂ in the solid solution are

$$a_{\text{LiF}}^{\text{S}} = X_{\text{LiF}}^{\prime(\text{S})} \cdot \gamma_{\text{LiF}}^{\text{(S)}} \quad (30)$$

$$a_{\text{MgF}_2}^{\text{S}} = \left(X_{\text{MgF}_2}^{\prime(\text{S})} \right)^2 \cdot \gamma_{\text{MgF}_2}^{\text{(S)}} \quad (31)$$

with $X_{\text{LiF}}^{\prime(\text{S})}$ and $X_{\text{MgF}_2}^{\prime(\text{S})}$ being the equivalent ionic fractions of LiF and MgF₂, respectively in the solid solution, i.e.

$$X_{\text{LiF}}^{\prime(\text{S})} = \frac{X_{\text{LiF}}^{\text{S}}}{1 + X_{\text{MgF}_2}^{\text{S}}} \quad (32)$$

$$X_{\text{MgF}_2}^{\prime(\text{S})} = \frac{2 X_{\text{MgF}_2}^{\text{S}}}{1 + X_{\text{MgF}_2}^{\text{S}}} \quad (33)$$

The activity coefficient of LiF in the solid solution in the LiF side of the phase diagram can be computed from equations (27), (28), and (30), and the activity coefficient of MgF₂ in the solid solution in the MgF₂ side of the phase diagram can be calculated from equations (27), (29), and (31). Knowledge of the activity coefficient of one component then can be used to determine the heat of mixing in the solid solutions with the assumption of a regular solution model (ref. 11). In this case the higher order terms in equation (5) are neglected and the heat of mixing per equivalent of the solution is

$$\Delta H_{\text{M}}^{\prime(\text{S})} = X_i^{\prime} (1 - X_i^{\prime}) \cdot A^{\prime} \quad (34)$$

For the regular solution approximation the activity coefficient is

$$RT \ln \gamma_i^{\text{(S)}} = (1 - X_i^{\prime})^2 \cdot A^{\prime} \quad (35)$$

and the heat of mixing/mole of solid solution is

$$\Delta H_{\text{M}}^{\text{S}} = \left(1 + X_{\text{MgF}_2}^{\text{S}} \right) \cdot \Delta H_{\text{M}}^{\prime(\text{S})} \quad (36)$$

From a knowledge of the activity coefficient of a component in a solution the constant "A" can be calculated; then the heat of mixing in the solid solution can be obtained from equations (34) and (36). With values for the heat of mixing in the liquid and the solid solutions, equation (24) can be utilized, and for LiF-MgF₂ eutectic at 1013 K the heat of fusion via this approach is 20.878 kJ/mole.

With the assumption of random mixing in both the liquid and solid phases and using the equivalent ionic fractions for the solid solutions, the entropy of fusion of the LiF-MgF₂ eutectic was calculated to be 26.5 J K⁻¹ mol⁻¹ which leads to a heat of fusion of 26.8 kJ/mole. Comparison of this estimate to that calculated from the heat of mixing considerations shows a large discrepancy (~25 percent) between the two methods which arises from the many assumptions necessary to compute the terms in equations (1) and (2).

KMgF₃-KCaF₃. - This system exhibits an eutectic equilibrium among liquid containing ~60 percent KCaF₃ and solid phases with 20 and 90 percent KCaF₃ at 1258 K (fig. 4). Since the heat capacity of the liquid and the constants in equation (4) for heat capacities of the solids are not known, the heat of fusion for KMgF₃ and KCaF₃ will be assumed to be independent of temperature. Similarly there exists no data for the heats of mixing for either the liquid or solid solutions; however they can be estimated from the phase diagram according to equations (9) to (12) and the assumptions that: (a) random mixing exists in all solutions, (b) the regular solution approximation holds for the melt, and (c) in the solid solutions Raoult's law is followed by the solvent and Henry's law is applicable to the solute. For the equilibrium between the eutectic melt and the KCaF₃ rich solid solution (β) equation (9) becomes

$$RT \ln \chi_{\text{KCaF}_3}^{e(l)} + \left(\chi_{\text{KMgF}_3}^{e(l)} \right)^2 \cdot A' - RT \ln \chi_{\text{KCaF}_3}^{\beta} = -\Delta G_{f, \text{KCaF}_3}^{o(T_e)} \quad (37)$$

The solution of equation (37) yields A' to be -556 J/mol. Thus the heat of mixing for the melt becomes

$$\Delta H_M^l = -556 \chi_{\text{KCaF}_3}^l \cdot \chi_{\text{KMgF}_3}^l \text{ J/mol} \quad (38)$$

From Raoult's law the activity of KMgF₃ in the KMgF₃ rich solid solution (α) is $\chi_{\text{KMgF}_3}^{\alpha}$; hence the thermodynamic equilibrium between the solid solutions α and β requires

$$\chi_{\text{KMgF}_3}^{\alpha} = \chi_{\text{KMgF}_3}^{\beta} \cdot \gamma_{\text{KMgF}_3}^{\beta} \quad (39)$$

Solution of equation (39) gives the activity coefficient of KMgF₃ in the KCaF₃ rich solid solution (β). Likewise the activity coefficient of KCaF₃ in the α solid solution can be determined. With a random distribution of cations, the heat of mixing/mole of each solid solution can be expressed as

$$\Delta H_M^{\alpha} = \chi_{\text{KCaF}_3}^{\alpha} \cdot RT \ln \gamma_{\text{KCaF}_3}^{\alpha} \quad (40)$$

$$\Delta H_M^{\beta} = \chi_{\text{KMgF}_3}^{\beta} \cdot RT \ln \gamma_{\text{KMgF}_3}^{\beta} \quad (41)$$

which when evaluated give 3.14 and 2.17 kJ/mol for α and β solid solutions, respectively. Substitution of the appropriate terms into equation (24) yields a heat of fusion for the KCaF₃-KMgF₃ eutectic of 58.6 kJ/mol. This can be

contrasted with a value of 65.7 kJ/mol which was determined from equation (25) assuming random mixing in all solutions.

NaMgF₃-KMgF₃. - While NaMgF₃ and KMgF₃ are completely soluble in one another (fig. 4) for both liquid and solid phases, the two phase equilibrium between liquid and solid possesses a minimum at 30 percent KMgF₃ and 1288 K where congruent melting takes place. Although no data exist for the heats of mixing in either the liquid or solid solutions, it is expected that $\Delta H_M^S > \Delta H_M^L > 0$ (ref. 17). An estimate of the heat of mixing for the solid solution can be obtained from the phase diagram and the assumption of ideal mixing for the melt: i.e., $\Delta H_M^L = 0$. With the further assumption that (a) the heat of fusion is independent of temperature, due to the lack of information on heat capacities, and (b) random mixing exists in the solid solution, equation (9) becomes

$$\Delta G_{f,NaMgF_3}^{o(1288\text{ K})} = 1288 R \cdot \ln \gamma_{NaMgF_3}^S \quad (42)$$

$$\Delta G_{f,KMgF_3}^{o(1288\text{ K})} = 1288 R \cdot \ln \gamma_{KMgF_3}^S \quad (43)$$

Thus the heat of mixing of the solid solution at $X_{KMgF_3} = 0.3$ is

$$\Delta H_M^{S(0.3\text{ KMgF}_3)} = 901 R \ln \gamma_{NaMgF_3}^S + 386 R \ln \gamma_{KMgF_3}^S \quad (44)$$

Combinations of equations (42) to (44) gives the heat of mixing for the solid solution at 30 mol percent KMgF₃ to be 1.4 kJ/mol, and this value can be substituted into the expression for the enthalpy of fusion

$$\Delta H_f^{0.3\text{ KMgF}_3} = 0.7 \Delta H_{f,NaMgF_3}^{1288\text{ K}} + 0.3 \Delta H_{f,KMgF_3}^{1288\text{ K}} - \Delta H_M^{S(0.3\text{ KMgF}_3)} \quad (45)$$

which yields a heat of fusion at the congruent melting point to be 70 kJ/mol.

Because the solid and liquid phases are of the same composition at the congruent melting point, the entropy of mixing would be the same for both liquid and solid solutions if random mixing is assumed. Therefore the entropy of fusion at the congruent melting point is given by

$$\Delta S_f^{0.3\text{ KMgF}_3} = 0.7 \Delta S_{f,NaMgF_3} + 0.3 \Delta S_{f,KMgF_3} \quad (46)$$

Evaluation of this equation yields 54.3 J K⁻¹ mol⁻¹ which converts to a heat of fusion of 70 kJ/mol from equation (2a).

Binary Eutectic Systems With Congruent Intermediate Compounds

Theory. - Figure 6 illustrates a binary system with one congruent melting compound at composition X_ϵ and two eutectics at X_{e1} and X_{e2} . Birchenall and Riechman (ref. 13) have outlined a method to estimate the heat of fusion for this type of system where there is negligible solid solubility of one component in the other. For the A-rich eutectic at X_{e1} , 1 mol of liquid upon freezing is converted to X_{e1} mol of compound ϵ and $(1 - X_{e1}/X_\epsilon)$ moles of pure A. Similarly for the B-rich eutectic at X_{e2} , 1 mol of liquid upon freezing is converted to $(1 - X_{e2})$ moles of the intermediate compound ϵ and $1 - \{(1 - X_{e2})/X_\epsilon\}$ moles of pure B. The heat of fusion/mole of the eutectic is given by

$$\Delta H_f^{e1} = (1 - X_{e1}) \Delta H_{f,A}^{Te1} + X_{e1} \Delta H_{f,B}^{Te1} + \Delta H_M^{e1(l)} - X_{e1} \Delta H_\epsilon^f \quad (47)$$

$$\Delta H_f^{e2} = (1 - X_{e2}) \Delta H_{f,A}^{Te2} + X_{e2} \Delta H_{f,B}^{Te2} + \Delta H_M^{e2(l)} - (1 - X_{e2}) \Delta H_\epsilon^f \quad (48)$$

where $\Delta H_M^{e1(l)}$ and $\Delta H_M^{e2(l)}$ are the heat of mixing of the eutectic liquid at compositions $e1$ and $e2$, respectively; ΔH_ϵ^f is the heat of formation for 1 mole of the intermediate compound ϵ from the components A and B.

Disregarding the entropy of mixing for the intermediate compound ϵ , the entropy of fusion/mole of the eutectic can be calculated in the same manner as binary eutectics without terminal solid solutions (eq. (17)). In general significant negative deviation would be expected in the liquid state for systems which form intermediate compound solid phases; thus the actual entropy of mixing should be lower than that calculated for an ideal solution. Because of this, the excess entropy of mixing must be taken into account; fortunately for systems where the heat of mixing is known, the excess entropy of mixing can be estimated from phase diagrams via equations (9) to (14).

NaF-MgF₂. - The compound NaMgF₃ is formed in the NaF-MgF₂ system (ref. 18) with eutectics forming on the NaF side of the phase diagram at 23 percent MgF₂ and 1103 K and on the MgF₂ side at 60 percent MgF₂ and 1273 K. Hong and Kleppa (ref. 8) have measured the heat of mixing of the NaF-MgF₂ melt at 1345 K for

$$0 < X_{MgF_2} < 0.7.$$

$$\Delta H_M^{NaF-MgF_2} = X_{NaF} \cdot X_{MgF_2} \left(-48.58 - 20.309 X_{MgF_2} + 8.732 X_{MgF_2}^2 \right) \text{ kJ/mol} \quad (49)$$

They also estimated the enthalpy of formation of NaMgF₃ to be -12.13 kJ/mol at 1300 K. Assuming that this value is unchanged by temperature, the heats of fusion of the two eutectics calculated from equations (47) and (48) are 29.8 kJ/mol of NaF-23MgF₂ and 38 kJ/mol of NaF-60MgF₂.

The experimental liquidus on the NaF side of the phase diagram and the eutectic point (60 percent MgF₂, 1273 K) on the MgF₂ side were used with the heat of mixing data (eq. (49)) to calculate the excess entropy of mixing via equations (9) to (14). From regression analysis

$$S_M^{E(\ell)} = X_{\text{NaF}} \cdot X_{\text{MgF}_2} \left(-18.99 - 47.23 X_{\text{MgF}_2} + 43.59 X_{\text{MgF}_2}^2 \right) \text{JK}^{-1} \text{mol}^{-1} \quad (50)$$

Combination of equation (50) with equation (17) to determine the entropies of fusion for the eutectic yields 28.4 JK⁻¹ mol⁻¹ and 31.15 JK⁻¹ mol⁻¹ for the NaF- and MgF₂-rich eutectics, respectively. Substitution of these values into equation (2a) gives the heats of fusion of 31.3 and 39.7 kJ/mol for the NaF- and MgF₂-rich eutectics, respectively. These values are in close agreement (~5 percent) with those calculated directly from the heat of mixing data.

KF-MgF₂. - The intermediate phase KMgF₃ forms an eutectic with KF at 1051 K at 14 percent MgF₂ and an eutectic with MgF₂ at 1281 K at 68.7 percent MgF₂ (ref. 19). The heat of mixing for KF-MgF₂ melt was found to be (ref. 8)

$$\Delta H_M^{\text{KF-MgF}_2(\ell)} = X_{\text{KF}} \cdot X_{\text{MgF}_2} \left[-63.082 - 64.751 X_{\text{MgF}_2} + 37.75 X_{\text{MgF}_2}^2 \right] \text{kJ/mol} \quad (51)$$

and the enthalpy of formation of KMgF₃ from KF and MgF₂ was estimated to be -22.6 kJ/mol at 1130 K. Assuming that the heat of formation for this compound is independent of temperature, as no data for the heat capacity of KMgF₃ exists; calculations based on equations (47) and (48) give 25.9 and 35.1 kJ/mol for the heats of fusion for the KF- and MgF₂-rich eutectics, respectively.

Estimation of the excess entropy of mixing along the liquidus curves for the KF-rich side of the phase diagram gave positive values which seem unreasonable in light of the strong interaction between KF and MgF₂, as evidenced by the large negative values for the heat of mixing. Because Hongand Kleppa's measurements ceased at X_{MgF₂} = 0.7, the required extrapolations to higher MgF₂ concentrations could lead to error in the entropy of mixing values; thus the excess entropy of mixing was calculated using only two points (50 and 68.7 mol percent MgF₂). From the literature (ref. 8) the entropy of fusion for KMgF₃ is 48.53 JK⁻¹ mol⁻¹ which is related by

$$\Delta S_{f, \text{KMgF}_3} = \Delta S_{f, \text{KF}} + \Delta S_{f, \text{MgF}_2} + 2 \Delta S_M^{\text{id}(0.5 \text{MgF}_2)} + 2 S_M^{E(0.5 \text{MgF}_2)} \quad (52)$$

to the entropies for KF and MgF₂ (ΔS_{f, KF} and ΔS_{f, MgF₂}) plus the excess and ideal entropies of mixing, ΔS_M^{0.5 MgF₂(id)} and S_M^{E(0.5 MgF₂)}, at the equimolar composition. After solving equation (52) for S_M^{E(0.5 MgF₂)} and combining this

expression with the excess entropy of mixing for 68.7 mol percent MgF_2 from equations (9) to (14), the excess entropy of mixing for the melt is

$$S_M^{E(\ell)} = X_{\text{KF}} \cdot X_{\text{MgF}_2} \left(-25.85 - 5.52 X_{\text{MgF}_2} \right) \text{JK}^{-1} \text{mol}^{-1} \quad (53)$$

From this equation and the entropies of fusion for KF and MgF_2 , equation (17) yields 23.6 and 27.5 $\text{JK}^{-1} \text{mol}^{-1}$ for the entropies of fusion of the KF- and MgF_2 -rich eutectics, respectively. In turn these values give (eq. (2a)) enthalpies of fusion of 24.8 and 35.2 kJ/mol for the respective eutectics which are in very good agreement with the values calculated directly from the heats of mixing.

KF-CaF₂. - The KF-CaF₂ system (ref. 20) has an intermediate compound at the equimolar composition which melts at 1343 K and possesses two eutectics: at 1055 K with 15 percent CaF₂ and at 1333 K with 62 percent CaF₂. Kleppa and Hong (ref. 6) have measured the heat of mixing for this system where

$$\Delta H_M^{\text{KF-CaF}_2(\ell)} = X_{\text{KF}} \cdot X_{\text{CaF}_2} \left(-33.848 + 1.799 X_{\text{CaF}_2} \right) \text{kJ/mol} \quad (54)$$

Neither the heats of formation nor fusion are known for KCaF_3 ; however these values can be estimated from the excess entropy of mixing. From the liquidus curves on both sides of the phase diagram, equations (9) to (14), and the heat of mixing expression (eq. (54)), the excess entropy of mixing in the melt is

$$S_M^{E(\ell)} = X_{\text{KF}} \cdot X_{\text{CaF}_2} \left(-13.8 + 1.51 X_{\text{CaF}_2} \right) \text{JK}^{-1} \text{mol}^{-1} \quad (55)$$

The entropy of fusion for KCaF_3 can be obtained from an expression modeled after equation (52) and is computed to be 50.85 $\text{JK}^{-1} \text{mol}^{-1}$; thus the enthalpy of fusion for this intermediate compound is 68.3 kJ/mol. The heat of formation of KCaF_3 from KF and CaF₂, $\Delta H_{\text{KCaF}_3}^f$, at its melting point can be calculated from

$$\Delta H_{\text{KCaF}_3}^f = \Delta H_{f,\text{KF}} + \Delta H_{f,\text{CaF}_2} + 2\Delta H_M^{0.5 \text{ CaF}_2(\ell)} - \Delta H_{f,\text{KCaF}_3} \quad (56)$$

and gives -19.53 kJ/mol.

The estimated heats of fusion for the two KF-CaF₂ eutectics were independent of the method of calculation and were obtained to be 27.6 kJ/mol for KF-15CaF₂ and 33.2 kJ/mol for KF-62CaF₂.

MF-AlF₃. - Three metal fluoride (M = Na, Li, or K) -AlF₃ phase diagrams have an intermediate compound M_3AlF_6 at 25 percent AlF₃ (refs. 21 to 23) which forms an eutectic with pure MF. As these systems have not been extensively studied beyond the M_3AlF_6 composition, only the MF-rich eutectics can be considered for energy storage applications. Because of its volatility, the melting point and heat of fusion for AlF₃ are not known; however Hong and

Kleppa (ref. 7) have estimated the heat of fusion to be 112 kJ/mol at 1298 K. Since the heat capacity data for liquid AlF_3 are not available, the enthalpy of fusion for this compound will be assumed to be independent of temperature. Heats of mixing for all three MF- AlF_3 systems have been measured by Hong and Kleppa (ref. 7) and their results are presented in figure 7. This data combined with the enthalpies of formation of M_3AlF_6 , as computed from the thermodynamic data in Barin and Knack's text (ref. 4), leads to the following heats of fusion for the three eutectics: 25.8 kJ/mol for NaF-14 AlF_3 at 1161 K, 28 kJ/mol for KF-6.8 AlF_3 at 1113 K, and 24.7 kJ/mol for LiF-14.5 AlF_3 at 983 K. Since the entropy of fusion of AlF_3 is not known, no attempt was made to calculate the heat of fusion via equations (17) and (2a).

TERNARY EUTECTIC SYSTEMS

The ternary system NaF- CaF_2 - MgF_2 exhibits two ternary eutectics (ref. 24) at NaF-27.2 CaF_2 -36.5 MgF_2 and 1178 K and at NaF-22.7 CaF_2 -12.8 MgF_2 and 1018 K which can be analyzed via equation (15). The heat of mixing for the NaF- CaF_2 and NaF- MgF_2 can be calculated from equations (23) and (49), respectively. No known data exists for the heat of mixing for CaF_2 - MgF_2 ; however with the assumption of the regular solution model, the heat of mixing can be calculated from the binary phase diagrams where

$$\Delta H_M^{CaF_2-MgF_2(l)} = -11.26 X_{CaF_2} \cdot X_{MgF_2} \text{ kJ/mol} \quad (57)$$

Substitution of the binary heat of mixing values along constant composition paths calculated from equations (23), (49), and (57) in equation (15) gives

the heat of mixing $\Delta H_{eM}^{NaF-CaF_2-MgF_2(l)}$ for the ternary eutectic melt. Use of

$\Delta H_{eM}^{NaF-CaF_2-MgF_2(l)}$ along with the heat of fusion of the individual components at the eutectic temperature in

$$\Delta H_{ef} = X_{NaF} \Delta H_{f,NaF}^{T_e} + X_{CaF_2} \cdot \Delta H_{f,CaF_2}^{T_e} + X_{MgF_2} \cdot \Delta H_{f,MgF_2}^{T_e} + \Delta H_{eM}^{NaF-CaF_2-MgF_2(l)} \quad (58)$$

yields the heat of fusion for the ternary eutectics to be 30.75 and 26.94 kJ/mol for NaF-27.2 CaF_2 -36.5 MgF_2 and NaF-22.7 CaF_2 -12.8 MgF_2 , respectively.

CONCLUDING REMARKS

In space power applications the heat of fusion per unit mass is probably more important than heat/mol since the energy storage media must be put into earth orbit. On the basis of literature data and thermodynamic calculations there appear to be a large number of fluoride systems (table III), including pure compounds and eutectic mixtures, which have relatively high enthalpies of fusion and melting points between 980 and 1378 K. Unfortunately no suitable systems have been identified between 1378 and the 1536 K melting point of MgF_2 .

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TABLE I. - THERMODYNAMIC DATA FOR PURE SALTS

| Compound | Melting point, K | Enthalpy of fusion, kJ/mol | Entropy of fusion, JK ⁻¹ mol ⁻¹ | The constants for the heat capacity of solid (eq. (4)), JK ⁻¹ mol ⁻¹ | | | Heat capacity of the melt, JK ⁻¹ mol ⁻¹ | Reference |
|--------------------------------|------------------|----------------------------|---|--|---------|---------|---|-----------|
| | | | | A | B | C | | |
| ^a CaF ₂ | 1691 | 29.706 | 17.568 (1424 to 1691 K) | 107.98 (1424 to 1691 K) | 10.46 | ----- | ----- | 4 |
| | | | 20.92 (<1424 K) | 59.83 (298 to 1424 K) | 30.459 | 1.966 | 99.997 | |
| KF | 1130 | 28.242 | 24.99 | 45.98 | 14.42 | ----- | 66.944 | 4 |
| LiF | 1121 | 27.196 | 24.254 | 42.689 | 17.417 | -5.3 | 64.18 | 4 |
| LaF ₃ | 1766 | 50.245 | 28.45 | 77.73 | 19.953 | ----- | 152.716 | 4 |
| MgF ₂ | 1536 | 58.157 | 37.86 | 70.83 | 10.543 | -9.2 | 94.43 | 4 |
| NaF | 1269 | 33.137 | 26.112 | 46.588 | 9.899 | -2.129 | 70.567 | 4 |
| ^b YF ₃ | 1428 | 27.97 | 19.585 (1350 to 1428 K) | -319.44 (1350 to 1428 K) | 212.798 | 2817.92 | ----- | 4 |
| | | | 43.60 (<1350 K) | 99.411 (<1350 K) | 7.426 | -5.69 | 133.662 | |
| KMgF ₃ | 1343 | 65.178 | 48.53 | ----- | ----- | ----- | ----- | 8 |
| NaMgF ₃ | 1303 | 74.14 | 56.9 | ----- | ----- | ----- | ----- | 8 |
| ^c KCaF ₃ | 1343 | 68.299 | 50.85 | ----- | ----- | ----- | ----- | - |

^aPhase change in solid at 1424 K, $\Delta H_{\text{trans}} = 4.769$ kJ/mol.

^bPhase change in solid at 1350 K, $\Delta H_{\text{trans}} = 32.426$ kJ/mol.

^cEnthalpy and entropy of fusion estimated from the present calculations.

TABLE II. - ESTIMATED HEATS OF FUSION FOR THE SIMPLE BINARY EUTECTIC SYSTEMS

[Compositions are in mole percent, e.g., A - mol percent B. NA - data on heat of mixing not available.]

| Composition, mole percent | Eutectic temperature, K | Heat of fusion estimated from equation (16), kJ/mol | Heat of fusion estimated from equation (17), kJ/mol | Heat of fusion estimated from equation (20), kJ/mol |
|--------------------------------------|-------------------------------|--|--|--|
| KF-40NaF | 994 | 28.233 | 29.2 | 29.15 |
| LiF-22CaF ₂ | 1039 | 27.86 | 28.17 | 28.47 |
| NaF-32CaF ₂ | 1083 | 28.04 | 30.95 | 30.35 |
| MgF ₂ -70YF ₃ | 1238 | NA | 58.5 | 54.8 |
| CaF ₂ -50MgF ₂ | 1253 | NA | 44 | 45.9 |
| MgF ₂ -37LaF ₃ | 1378 | NA | 54.9 | 48.5 |

TABLE III. - HEAT OF FUSION PER UNIT MASS FOR SEVERAL
FLUORIDE SALTS

| Composition, mole percent | Temperature, K | Heat of fusion, kJ/gm |
|---|-------------------|--------------------------|
| LiF-14.5AlF ₃ | 983 | 0.721 |
| NaF-60KF | 994 | .546 to 0.564 |
| LiF-33MgF ₂ | 1013 | .55 to 0.7 |
| NaF-22CaF ₂ -13 MgF ₂ | 1018 | .51 |
| LiF-22CaF ₂ | 1039 | .745 to 0.761 |
| KF-14MgF ₂ | 1043 | .42 to 0.44 |
| KF-15CaF ₂ | 1055 | .452 |
| Li ₃ AlF ₆ | 1059 | .54 |
| NaF-32CaF ₂ | 1083 | .52 to 0.56 |
| NaF-23MgF ₂ | 1103 | .64 to 0.67 |
| KF-6.8AlF ₃ | 1113 | .47 |
| LiF | 1118 | a ₁ .087 |
| KF | 1129 | a.486 |
| NaF-14AlF ₃ | 1161 | .539 |
| NaF-27CaF ₂ -36 MgF ₂ | 1178 | .52 |
| MgF ₂ -70YF ₃ | 1238 | .45 to 0.48 |
| CaF ₂ -50MgF ₂ | 1253 | .61 to 0.65 |
| KCaF ₃ -40KMgF ₃ | 1258 | .45 to 0.5 |
| NaMgF ₃ -30KMgF ₃ | 1259 | .641 |
| K ₃ AlF ₆ | 1263 | a.47 |
| NaF | 1268 | a.789 |
| NaF-60MgF ₂ | 1273 | .7 to 0.732 |
| KF-68.7MgF ₂ | 1281 | .57 to 0.58 |
| Na ₃ AlF ₆ | 1283 | a.53 |
| NaMgF ₃ | 1303 | b.711 |
| KF-62CaF ₂ | 1333 | .47 |
| KMgF ₃ | 1343 | b.541 |
| KCaF ₃ | 1343 | .501 |
| FeF ₂ | 1373 | a.553 |
| MgF ₂ -37LaF ₃ | 1378 | .43 to 0.49 |
| MgF ₂ | 1536 | a.933 |

aObtained from reference 4.

bObtained from reference 8.

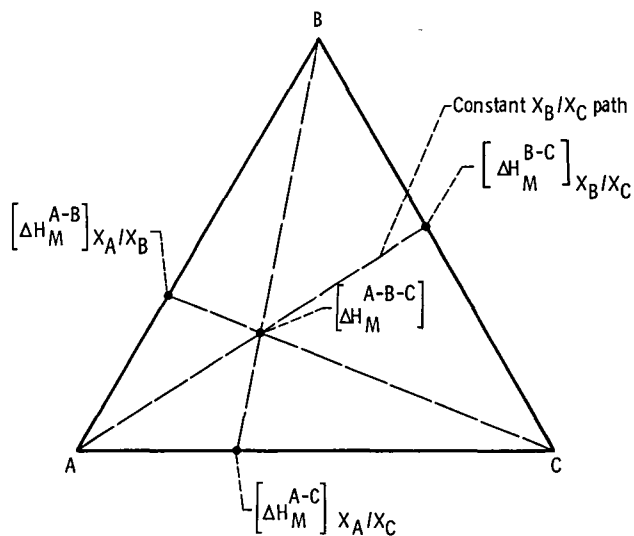


Figure 1. - Definition of terms used to calculate the enthalpy of mixing for ternary liquid solutions from binary heat of mixing data.

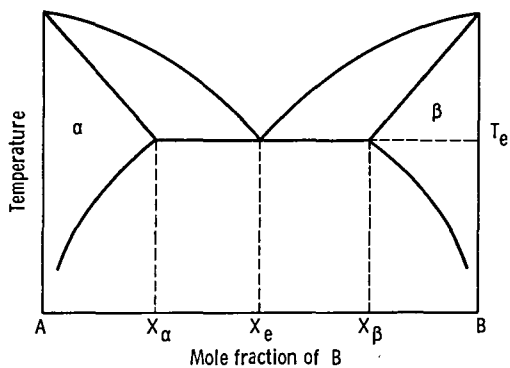


Figure 2. - Schematic of a phase diagram having a single eutectic with terminal solid solutions.

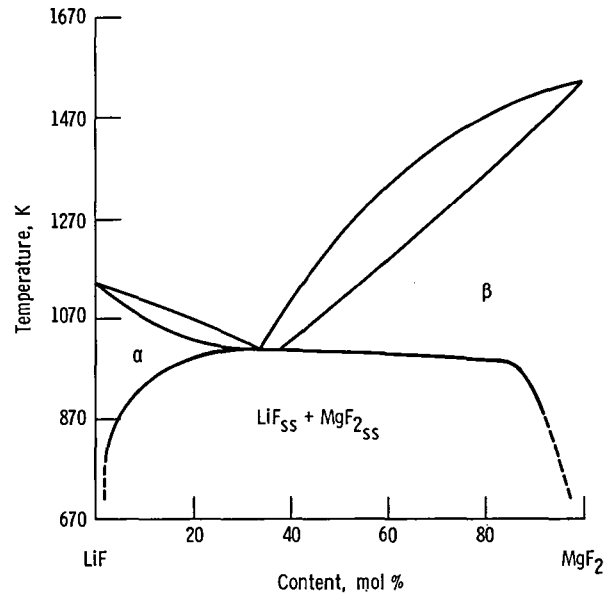


Figure 3. - LiF - MgF₂ phase diagram (ref. 14).

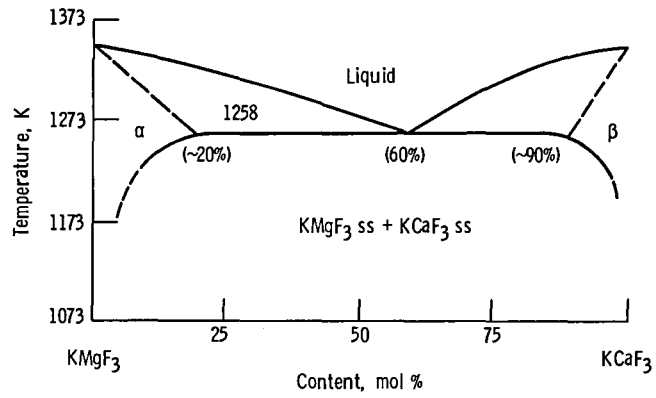


Figure 4. - KMgF₃ - KCaF₃ phase diagram (ref. 15).

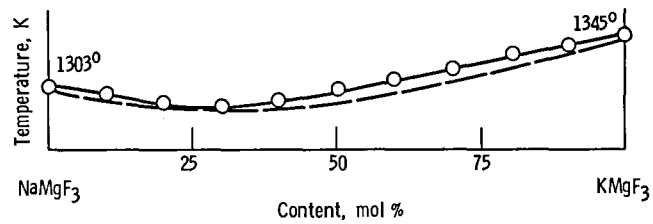


Figure 5. - NaMgF₃ - KMgF₃ phase diagram (ref. 16).

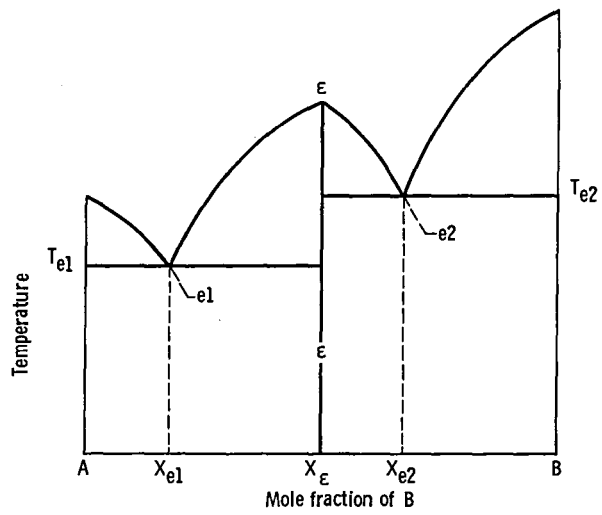


Figure 6. - Schematic of a phase diagram with a congruently melting intermediate compound and two eutectics.

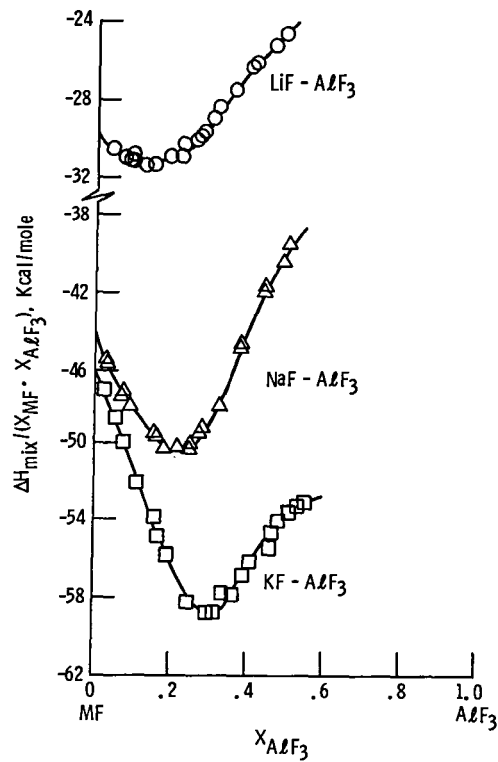


Figure 7. - Heat of mixing for MF - AlF₃ melts (ref. 7) where M is Na, K or Li.

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| 15. Supplementary Notes Ajay K. Misra, Case Western Reserve University, Dept. of Metallurgy and Materials Science, Cleveland, Ohio 44106 and NASA Resident Research Associate; John D. Whittenberger, NASA Lewis Research Center. | | | |
| 16. Abstract <p>The heats of fusion of several fluoride salt mixtures with melting points greater than 973 K have been estimated from a coupled analysis of the available thermodynamic data and phase diagrams. Simple binary eutectic systems with and without terminal solid solutions, binary eutectics with congruent melting intermediate phases, and ternary eutectic systems were considered. Several combinations of salts have been identified, most notably the eutectics LiF-22CaF₂ and NaF-60MgF₂ which melt at 1039 and 1273 K respectively which possess relatively high heats of fusion/gm (>0.7 kJ/g). Such systems would seemingly be ideal candidates for the light weight, high energy storage media required by the thermal energy storage unit in advanced solar dynamic power systems envisioned for the future space missions.</p> | | | |
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