A MODEL AND DATA FOR - 
FREEZING TEMPERATURE LOWERING OF 4 TO 7 
COMPONENT MOLTEN SALT MIXTURES 

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ABSTRACT 

Research was conducted to find molten salt mixtures, compatible with alkali metal sulfates, as media for ammonium hydrogen sulfate reactions. Mixtures of mono- and divalent metal sulfates having freezing temperatures of \( \sim 550 \) K were sought, pure sulfates melt at 1000 to 1300 K. Nine divalent metal sulfates with three alkali metal sulfates were used. 

For interpretation of experimental data a thermodynamic model was developed, the key parameter being the "excess entropy-enthalpy function", positive values of the excess function produce greatest effect. Results gave for 4-components 640 K; for 5-components 631 K; for 6-components 596 K; and 7-components 593 K. 

INTRODUCTION 

The Ammonium-Hydrogen-Sulfate (AHS) energy storage cycle was proposed 11 years ago by Wentworth and Chen (1), followed by process configurations proposed by Prengle and coworkers (2,3). The duplex modification of the cycle proposed by Prengle in 1984 is based on conducting the two endothermic chemical reactions (4) in a compatible molten salt (CMS) mixture. The first reaction (450-600 K) produces \( \text{NH}_3 \), \( \text{H}_2\text{O} \), and \( \text{S}_2\text{O}_7^{2-} \) by reaction of ammonium hydrogen sulfate with an alkali metal sulfate, and the second (650-950 K) produces \( \text{SO}_3 \) by decomposition of the pyrosulfate. The duplex version of the cycle contemplates using the sensible energy in the excess CMS immediately; whereas the exothermic recombination of the three product molecules would be accomplished for later use of the stored energy. 

The research described in this paper concerns the search for CMS mixtures of alkali metal, alkaline earth, and transition metal sulfates which could be used as reaction media for the two reaction steps mentioned above. Specifically, the objective of the work was to discover mixtures of mono- and divalent metal sulfates with freezing temperatures of \( \sim 550 \) K, a significant lowering as the pure components melt.
in the range of 1000-1300 K.

**LITERATURE SEARCH**

Data on thirty-two sulfate eutectic mixtures were obtained from the literature (5,6,7), including the alkali metal components Li, Na, K, the alkaline earths Mg, Ca, Ba, and the transition metals Zn, Cu, Cd, Pb, Co and Mn. It was hoped that some preliminary answers would be revealed to the three questions: -the possible amount of freezing temperature lowering, -the effect of specific metal ions, and -the number required to get 500-600 degree lowering.

By analogy with the thermodynamic mixing property, a preliminary lowering criterion can be defined. For example, for a local minimum enthalpy, the mixing property, $\Delta H^M$, will be,

$$\Delta H^M = \sum X_i (H_i - \bar{H}_i)$$  \hspace{1cm} (1)

where $X_i$, $H_i$, $\bar{H}_i$, are the mole fraction, partial mole enthalpy, and pure component enthalpy respectively. Similarly, for a molten salt eutectic mixture freezing temperature will be,

$$\Delta T_f = \sum X_i (T_f - T_{f1})$$  \hspace{1cm} (2)

and,

$$\sum X_i (T_f - T_{f1}) / \Delta T_f = \sum X_i \xi_i = 1$$  \hspace{1cm} (3)

each term in the series representing the fraction lowering, $\xi_i$, of the freezing temperature for a given component. Using this method of analysis, Table 1 presents the results for mixtures of alkali metal and alkaline earth sulfates, indicating that in a preliminary way Li had the greatest effect, K was next highest, and Na and Ba were lowest.

The remaining eighteen mixtures of alkali metal sulfates with Group IB, IIB and VIB, VIIB and VIII were analyzed similarly. As a preliminary guide to further experimental work, the final ranking of the components, based on all thirty-two mixtures, in descending order with some overlap was,

$$\xi(Li) > \xi(K) > \xi(Zn) > \xi(Mg)$$

$$\xi(Pb) > \xi(Cd) > \xi(Ca) > \xi(Na) > \xi(Ba)$$

$$\xi(Cu) > \xi(\text{Co}) > \xi(Mn)$$
Table 1 - Contributions of Alkali Metal and Alkaline Earths

| Mixture | $\xi_a$ (Li) | $\xi_b$ (Na) | $\xi_c$ (K) | $\xi_d$ (Mg) | $\xi_e$ (Ca) | $\xi_f$ (Ba) |
|---------|--------------|--------------|-------------|--------------|--------------|--------------|
| L1      | 0.636        | 0.564        | -           | -            | -            | -            |
| L2      | 0.748        | -            | 0.2523      | -            | -            | -            |
| L3      | -            | 0.345        | 0.655       | -            | -            | -            |
| L4      | 0.744        | 0.084        | 0.172       | -            | -            | -            |

Conclusion: $\xi_a > \xi_c > \xi_b$

| L12     | -            | -            | 0.623       | 0.377        | -            | -            |
| L8      | -            | -            | 0.482       | -            | 0.518        | -            |
| L7      | -            | -            | 0.520       | -            | -            | 0.480        |
| L20     | 0.657        | -            | -           | 0.343        | -            | -            |
| L17     | 0.687        | -            | -           | -            | 0.313        | -            |
| L16     | 0.502        | -            | -           | -            | -            | 0.498        |
| L28     | -            | -            | 0.483       | -            | 0.592        | 0.125        |
| L30     | -            | -            | 0.186       | 0.748        | 0.066        | -            |
| L29     | -            | 0.255        | -           | -            | 0.585        | 0.160        |
| L32     | -            | 0.320        | 0.334       | 0.342        | -            | -            |

Conclusion: $\xi_a > \xi_c > \xi_d > \xi_e > \xi_b > \xi_f$

**EXPERIMENTAL**

The search to find the desired 550 K freezing temperature mixture(s) resulted in measurements on 45 four-seven component mixtures of Li$,^+$, Na$,^+$, K$,^+$ sulfates with Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$ alkaline earth sulfates, and seven transition metal sulfates, Cd$^{2+}$, Co$^{2+}$, Cr$^{2+}$, Cu$^{2+}$, Mn$^{2+}$, Pb$^{2+}$, and Zn$^{2+}$. The sulfates used were reagent grade of 99% purity. Mixtures of known composition were made up, melted, and held in liquid phases for ~12 hours to insure ionic equilibrium, prior to determination of the cooling curve by electrical conductivity.

Figure 1 displays a typical conductivity-temperature plot, as $\ln \lambda$ vs. $1/T$, indicating an observed hysteresis cooling-heating curve. Since primary interest is in the occurrence of solidification from the liquid phase, the values of $T_0$ and $T_f$ were taken as more meaningful to the objectives of the project. Simultaneously the cooling curve derivative was determined and recorded electronically, displayed in Figure 2, permitting a more precise determination of the difference $\Delta T = T_0 - T_f$. This difference was used as a guide for successive estimation of new compositions closer to the eutectic point. Details of the equipment
used are presented by Shah (8).

**T**\(_f\)-LOWERING MODEL

As the experimental work progressed it was apparent that a model for calculation of the excess entropy and enthalpy was needed to guide the composition choices, a criterion more precise than the ξ\(_i\) ordering. Consider the T-S loop cycle shown in Figure 3, starting with the pure components in the solid phase of a eutectic mixture. As the solid phase is heterogeneous a generalized composition dependent structure is not possible; instead the pure components were chosen arbitrarily as the starting point. Progressing around the cycle, points 1 to 4, the sum of the entropy terms and the corresponding enthalpy terms, are given by

\[
\sum_i x_i \bar{C}_{pi} \ln \frac{T^*_f}{T_f} + \Delta S^*_m + \Delta S^*_L + \sum_i x_i \bar{C}_{pLi} \ln \frac{T^*_f}{T} - \Delta S_m = 0 \quad (4a)
\]

\[
\sum_i x_i \bar{C}_{pi} (T^* - T_f) + \Delta H^*_m + \Delta H^*_L + \sum_i x_i \bar{C}_{pLi} (T_f - T^*) - \Delta H_m = 0 \quad (4b)
\]

where \(\Delta S_m = \sum x_i \Delta S_{m_i}\), \(\Delta H_m = \sum x_i \Delta H_{m_i}\), and \(T^* = \Delta H^*_m / \Delta S^*_m\). Solving for \(\Delta S_m\) and \(\Delta H_m\) gives,

\[
\Delta S_m (at T_f) = \Delta S^*_m + \Delta S^*_L + \langle \Delta C_p \rangle \ln \frac{T^*_f}{T_f} \quad (4c)
\]

\[
\Delta H_m (at T_f) = \Delta H^*_m + \Delta H^*_L + \langle \Delta C_p \rangle (T^* - T_f) \quad (4d)
\]

where, \(\langle \Delta C_p \rangle \equiv \sum x_i \bar{C}_{pi} - \sum x_i \bar{C}_{pLi}\), the difference between the crystal and liquid heat capacities. Combining by \(T_f \Delta S_m = \Delta H_m\) gives,

\[
T_f \Delta S^*_m + T_f \Delta S^*_L + T_f \langle \Delta C_p \rangle \ln \frac{T^*_f}{T_f} = \Delta H^*_m + \Delta H^*_L + \langle \Delta C_p \rangle (T^* - T_f) \quad (5a)
\]

The two heat capacity terms can be combined, letting

\[
g = T_f \langle \Delta C_p \rangle \ln \frac{T^*_f}{T_f} - \langle \Delta C_p \rangle \frac{(T^* - T_f)}{T_f} = T_f \langle \Delta C_p \rangle \ln \left(\frac{T^*_f}{T_f} + \frac{\Delta T}{T_f}\right) - \left(\frac{T_f + \Delta T - T_f}{T_f}\right)
\]

\[
g = T_f \langle \Delta C_p \rangle \ln \left(1 + \frac{\Delta T}{T_f}\right) - \frac{\Delta T}{T_f} \quad (5b)
\]

also letting, \(y = \frac{\Delta T}{T_f}\); \(g = T_f \langle \Delta C_p \rangle \ln \left(1 + y\right) - y\); \(y \approx 0.10\) to \(0.50\),

\[
\ln \left(1 + y\right) - y \approx y - ay^2 - y = -ay^2 = -a \left(\frac{\Delta T}{T_f}\right)^2 \quad (5c)
\]

where \(a = 0.422 \pm 0.037\), and \(g = -ay^2 \langle \Delta C_p \rangle / T_f\).
Substituting into 5a and solving for $T_f$ gives,

$$T_f = \frac{\Delta H_m^* (1 + H_L^E / \Delta H_m^* )}{\Delta S_m^* [1 + \frac{1}{\Delta S_m^*} (\Delta S_L^M - a y^2 \langle \Delta C_p \rangle)]}$$

Letting $u_1 \equiv H_L^E / \Delta H_m^* ; u_2 \equiv [\Delta S_L^M - a(\frac{\Delta T}{T_f})^2 \langle \Delta C_p \rangle] / \Delta S_m^*$

then, $T_f = \Delta H_m^* (1 + u_1) / \Delta S_m^* (1 + u_2) = T^* (1 + u_1)/(1 + u_2) = T^* \theta$

or, $\theta = \frac{T_f}{T^*} = (1+u_1)/(1+u_2) = 1 - u_1 - u_2 + [\text{higher order terms}]$

The quantity of interest is the fraction depression of $T^*$, called $\alpha = (1-\theta)$. Neglecting the higher order terms gives,

$$\alpha \approx u_2 - u_1 = \frac{1}{\Delta S_m^*} (\Delta S_L^M - a y^2 \langle \Delta C_p \rangle) - H_L^E / \Delta H_m^*$$

Inserting the ideal entropy of mixing and the excess entropy, $y^2$ in terms of $\alpha$, and defining $\phi^E \equiv (S_L^E - H_L^E / T^*)$ gives the model equation,

$$\alpha = \frac{R}{\Delta S_m^*} (- \Sigma x_i \ell_n x_i) + \phi^E / \Delta S_m^* - a(\frac{\alpha}{1 - \alpha})^2 \langle \Delta C_p \rangle / \Delta S_m^*$$

The magnitude of the excess property function, $\phi^E$, being determined primarily by the liquid phase excess entropy, which can be positive or negative depending on the liquid phase molecular configuration. For a given experimental mixture, knowing $\alpha$, $\langle \Delta C_p \rangle$, and $\Delta S_m^*$, the value of the excess function can be obtained,

$$\phi^E = \alpha \Delta S_m^* + \text{RE} x_i \ell_n x_i + a(\frac{\alpha}{1 - \alpha})^2 \langle \Delta C_p \rangle$$

It is obvious that a positive excess function is desirable to obtain larger $\alpha$-values.

THE CORRELATION PAIR

As a consequence of the model, combined with a Scatchard function, a correlation pair results for the freezing temperature lowering as a function of the thermodynamic variables. Examination of the $\alpha$-function (Eqn. 6b) indicates that it is a cubic-in-$\alpha$ for which the real root $0<\alpha<1$ is desired, and in this region can be represented by a quadratic rather than a cubic. Defining,

$$w \equiv \Delta S_m^*/\langle \Delta C_p \rangle, \text{ and } z \equiv (\phi^E - \text{RE} x_i \ell_n x_i) / \Delta S_m^*$$

followed by mathematical simplification of 6b leads to the dimensionless form,
\[ \alpha = 7(zw)^{1/6} - \frac{\alpha}{w} \]  
\[ \alpha/w = 7(z/w)^{1/6} - 1/6 \]  
(7b)  
(7c)

Neither equations 6c or 7a,b are predictive of \( \phi^E \), both requiring experimental data; however, once a few values of the excess function are known as a function of composition for a particular group of mixtures, a pseudo-binary Scatchard (9) function can be used to correlate the values,

\[ \phi^E = X_1 X_2 A_0 [1 + a_1 (X_1 - X_2) + a_2 (X_1 - X_2)^2 + ...] \]  
(7d)

Equations 7a or b and 7d constitute the correlation pair of equations. For the case of sulfate mixtures, \( X_1 \) and \( X_2 \) were taken as \( X^m \) and \( X^d \), the mole fractions of the mono- and divalent metal sulfates respectively.

RESULTS

Using model equation 6c, values of the excess function were calculated for the thirty-two literature and the forty-five experimental mixtures. For the divalent metals with alkali metal sulfates, some gave positive values others negative values as indicated,

| positive \( \phi^E \) values | negative \( \phi^E \) values |
|-----------------------------|-----------------------------|
| barium                      | 75%                         | cadmium                      | 78%                         |
| calcium                     | of all                      | cobalt                       | of all                      |
| lead                        | positive                    | copper                       | negative                    |
| zinc                        | values                      | magnesium                    | values                      |
|                             |                             | manganese                    |                             |

A test of the \( \alpha \)-correlation is presented as Figure 4 for the literature plus experimental mixtures with positive excess function values. The computer generated curve as \( f(zw) \) gives a very good fit, \( r=0.985 \).

The positive \( \phi^E \)-values were correlated as suggested by a Scatchard function giving,

\[ \phi^E (J/gmol K) = A_0 X_m X_d [1 + a_1 (X_m^m - X_d) + a_2 (X_m^m - X_d)^2] \]
\[ = 3.064 X_m X_d [1 + 1.559 (X_m^m - X_d) + 16.99 (X_m^m - X_d)^2] \]  
(8a)

\( r = 0.990 \)

Plots of \( \phi^E / X_m X_d \) vs. \( (X_m^m - X_d) \) and \( \phi^E \) vs. \( X_m^m \) are shown as Figures 5a,b, the latter plot indicating that greatest temperature lowering should occur in the vicinity of \( X = 0.20 \) and 0.80.

As regards our experimentally measured freezing temperatures, two
ternary mixtures reported in the literature (4,6) served as the lowest temperature starting point: 1) -an alkali metal sulfate mixture, X(Li) 0.780, X(Na) 0.085, X(K) 0.135, T_f = 785 K; and 2) -a mixture with zinc sulfate, X(Na) 0.190, X(K) 0.258, X(Zn) 0.552, T_f = 661 K, the effect of zinc being rather striking. Table 2 summarizes the 'best' 4, 5 and 7 component mixtures, and Figure 6 is a plot showing the convergence of 6-component mixtures to eutectic compositions.

Table 2. Lowest T_f for 4, 5, and 7 Component Mixtures

| N | Composition   | X_1 | X_m | α   | T* K | T_f |
|---|---------------|-----|-----|-----|------|-----|
| 4 | (Li) 0.3247   | (Na) 0.1579 |   |     |      |     |
|   | (K) 0.0741    | (Zn) 0.4433 |   |     |      |     |
|   |               | 0.5567 | 0.4123 | 1103 | 649  |
| 5 | (Li) 0.3268   | (Na) 0.1586 |   |     |      |     |
|   | (K) 0.0746    | (Zn) 0.3556 |   |     |      |     |
|   | (Ca) 0.0842   |               |   |     |      |     |
|   |               | 0.5602 | 0.4550 | 1158 | 631  |
| 7 | (Li) 0.1600   | (Na) 0.2600 |   |     |      |     |
|   | (K) 0.2600    | (Ca) 0.0150 |   |     |      |     |
|   | (Ba) 0.0100   | (Mg) 0.0885 |   |     |      |     |
|   | (Zn) 0.2065   |               |   |     |      |     |
|   |               | 0.6800 | 0.5220 | 1221 | 593  |

The research to date has achieved T_f values in the vicinity of 590 K, lower values should follow with additional work.

DISCUSSION

Three items are believed to be significant from the work, the fact that: 1) -the mixture freezing point can be reduced more than 50% of the linear combination freezing point, 2) -the proposed model can be used to guide the search to the composition regions where greatest lowering can be expected, and 3) -statistically the mono- and divalent sulfate mixtures involved showed significant excess entropy and enthalpy. Concerning the latter matter, Lumsden (11) and Bloom (12), following Hildebrand (10) have viewed molten salt mixtures as 'regular' solutions; however, it was expected that the mixtures investigated in this work would show excess entropy. The choice of the definition of the excess function, \( \phi^E = S^E - H^E/T^* \), was a matter of mathematical convenience, as individually \( S^E \) and \( H^E \) can not be separated. Those mixtures with positive excess function showed values of \( 0 < \phi^E < 4 \), J/gmol K, which is considered to be primarily entropy, as enthalpy is small when divided by \( T^* \).
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Fig. 1. Dynamic Hysteresis

Fig. 2. Typical Derivative

Fig. 3. T-S Cycle

Fig. 4. Temperature Lowering Correlation
Fig. 5A, B. Excess Function Correlation

Fig. 6. Freezing Temperature Convergence