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CALORIMETRIC DETERMINATION OF THE THERMODYNAMIC PROPERTIES OF THE BINARY EUTECTICS IN THE $NaNO_3$—$Ca(NO_3)_2$ AND KNO_3—$Ca(NO_3)_2$ SYSTEMS

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ABSTRACT

The enthalpies of the binary eutectic solutions 0.701 $NaNO_3 \cdot 0.299\ Ca(NO_3)_2$ and 0.667 $KNO_3 \cdot 0.333\ Ca(NO_3)_2$ were determined for the solid and liquid states by drop calorimetry. For the $NaNO_3$—$Ca(NO_3)_2$ system, the results gave a heat of fusion of about 3.4 kcal $mole^{-1}$; the molar enthalpy for this system in the liquid state (525—500 K) is given by (42.42T—10974) cal $mole^{-1}$ with a standard deviation of 190 cal $mole^{-1}$. In the KNO_3—$Ca(NO_3)_2$ system, the heat of fusion equals approximately 2.2 kcal $mole^{-1}$, and the molar enthalpy in the liquid state (439—616 K) is given by (41 71T—11691) cal $mole^{-1}$ with a standard deviation of 150 cal $mole^{-1}$. The results are shown to be in good agreement with heat of solution work by Kleppa and Hersh and are used with the results of these workers to estimate the molar enthalpy of supercooled liquid $Ca(NO_3)_2$ at 18 kcal $mole^{-1}$ (623 K).

INTRODUCTION

Many of the data tabulated in the literature on the use of the heat of fusion of inorganic salt eutectics for energy storage purposes are calculated. With this in mind, for some time now, we have been engaged in producing experimental values for systems that could be of interest in the context of energy storage, particularly at the relatively low temperature end of the scale. We have tended to confine ourselves to salt systems that are inexpensive, have melting points below 400° C, and are fairly easy to contain.

While our primary motives have been to measure heats of fusion and to observe any difficulties that would preclude the use of the salt system for the purpose envisaged, an important secondary motive has been to contribute to the general literature on molten salt systems whenever possible. The present paper is such an example.

Nitrate or nitrate containing systems are attractive in the present context, but the heats of fusion of pure nitrates are relatively low [1]. The usefulness of a eutectic composition will be limited, despite its very low melting temperature, if the heat of fusion is too low. Various methods of estimating heats of fusion of eutectics have been proposed [2] but they assume ideal mixing behavior, i.e. the heat of mixing is zero. Thus the heat of fusion could be higher or lower than predicted.

In the case of the eutectics formed by $Ca(NO_3)_2$ with the alkali metal nitrates $NaNO_3$ and KNO_3, however, it is not possible even to estimate the heats of fusion since virtually no data are available for $Ca(NO_3)_2$ apart from an extrapolated heat of fusion to supercooled liquid at 350° C [3].

Many contributions have been made to the thermodynamics of molten salt solutions by Kleppa [4] and various collaborators. Some years ago, in considering mixtures of salts with different charge structures but with a common ion, Kleppa and Hersh [3] measured calorimetrically the heats of solution of solid calcium nitrate in liquid alkali nitrates at 350° C. In the present paper, we show how Kleppa's heats of mixing and our enthalpy measurements are consistent with each other. We also show how the two sets of data can be used to calculate an approximate value for the enthalpy of supercooled liquid $Ca(NO_3)_2$ at 623 K.

EXPERIMENTAL

The calorimetric method has been described elsewhere [2]. Analytical grade reagents were used. The $NaNO_3$ and KNO_3 were dried at about 380 K before use. The $Ca(NO_3)_2 \cdot 4\,H_2O$ was dehydrated by heating in vacuum, with the temperature raised slowly to about 420 K; this procedure avoids formation of CaO.

Enthalpy measurements were made at the eutectic compositions in the systems $NaNO_3$—$Ca(NO_3)_2$ and KNO_3—$Ca(NO_3)_2$ as read from the phase diagrams in "Phase Diagrams for Ceramists" [5] (it was recognized that these values might not be exact). The compositions were taken as $0.701\ NaNO_3 \cdot 0.299\ Ca(NO_3)_2$ and $0.667\ KNO_3 \cdot 0.333\ Ca(NO_3)_2$, with eutectic temperatures at 505 and 417 K, respectively.

RESULTS

The results are summarized in Fig. 1. Obviously, modest heats of fusion are available for storage purposes, approximately 3.4 kcal mole^{-1} (~31 cal g^{-1}) and 2.2 kcal mole^{-1} (~17 cal g^{-1}) for the $NaNO_3$—$Ca(NO_3)_2$ and KNO_3—$Ca(NO_3)_2$ eutectics, respectively. These compare with 3.44 kcal mole^{-1} (40.5 cal g^{-1}) and 2.15 kcal mole^{-1} (21.3 cal g^{-1}) for $NaNO_3$ and KNO_3 as measured recently [2]. It should be noted, however, that these somewhat smaller heats of fusion are available for use at considerably lower temperatures, particularly in the case of the KNO_3 containing eutectic.

Some difficulty with glass formation was encountered with the KNO_3—$Ca(NO_3)_2$ system when the samples were equilibrated at temperatures around the fusion temperature in readiness for the calorimetry. As a result, it is not certain how much the ill-defined enthalpy increase in the region of the fusion temperature is due to a slightly wrong composition and how much it is due to the solid phase being glassy. Fortunately, the usual rapid cooling occurring when the liquid sample was lowered in the calorimeter always resulted in crystalline material.

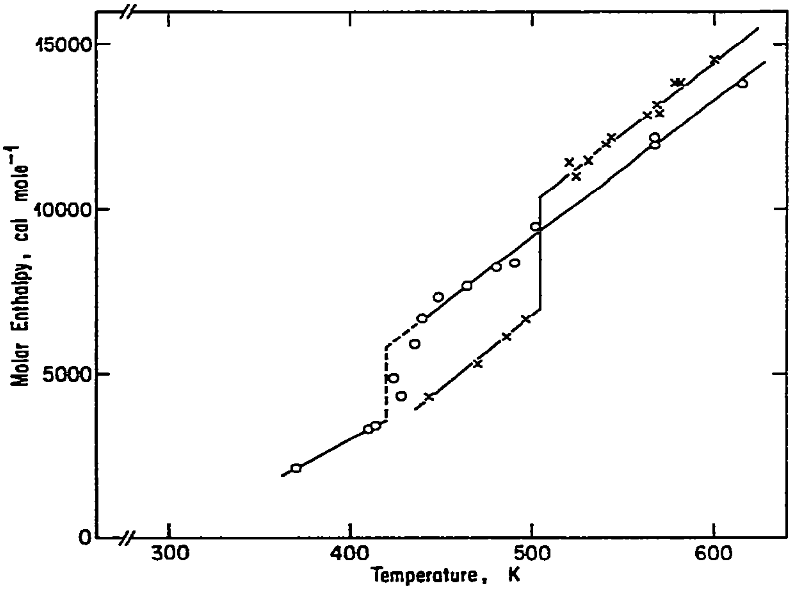

Fig. 1. Molar enthalpies of the solutions 0.701 $NaNO_3 \cdot 0.299\ Ca(NO_3)_2$ and 0.699 $KNO_3 \cdot 0.301\ Ca(NO_3)_2$. ×, $NaNO_3$—$Ca(NO_3)_2$, ⊙, KNO_3—$Ca(NO_3)_2$.

Regression equations were calculated to express the results for the liquid state in terms of variation of molar enthalpy as a function of temperature. For 0.701 $NaNO_3 \cdot 0.299\ Ca(NO_3)_2$ the equation is

$$\Delta h_{T(Na-Ca)} = (42.42T - 10974) \text{ cal mole}^{-1} \tag{1}$$

for the temperature range 525—600 K, with a standard deviation of 190 cal mole^{-1}. For 0.667 $KNO_3 \cdot 0.333\ Ca(NO_3)_2$ it is

$$\Delta h_{T(K-Ca)} = (41.71T - 11691) \text{ cal mole}^{-1} \tag{2}$$

for the temperature range 439—616 K, with a standard deviation of 150 cal mole^{-1}. As defined in an earlier paper [2], $\Delta h_T = (H_T - H_{T_3})$, where T is the temperature at which the enthalpy is measured and T_3 is the final temperature reached in the calorimeter. In other words, Δh_T is the molar enthalpy referred to a temperature that is close to but not at 298 K. It is considered that the difference between Δh_T and the more usual $(H_T - H_{298})$ is, for most purposes, negligibly small.

DISCUSSION

At a temperature above the melting points of the end members, the heat of mixing of a binary solution can be represented by the equation

$$\Delta H_M = (H_T - H_{298})_{\text{sol,liq}} - \chi_A(H_T - H_{298})^*_{A,\text{liq}} - \chi_B(H_T - H_{298})^*_{B,\text{liq}} \tag{3}$$

where, ΔH_M = molar heat of mixing, χ_A, χ_B = mole fraction of A and B in the solution, and $(H_T - H_{298})^*_A$, $(H_T - H_{298})^*_B$ = molar enthalpy of pure A and pure B.

At temperatures below the melting points of the end members, the enthalpy terms will be those for the supercooled liquids. Thus, this heat of mixing is not the same as ΔH^{M} in Kleppa's paper [3]. Kleppa's ΔH^{M} is the heat of formation of the salt melt at 623 K from pure liquid alkali nitrate and pure solid calcium nitrate. Thus, in addition to the heat of mixing it includes $\Delta H_{F,Ca(NO_3)_2}$, the heat of fusion of calcium nitrate at 623 K to supercooled liquid. Hence

$$\Delta H^{M} = \Delta H_{M} + \chi_{Ca(NO_3)_2}\,\Delta H_{F,Ca(NO_3)_2} \tag{4}$$

Kleppa's experimental values for lithium, sodium, potassium and rubidium nitrates with calcium nitrate were plotted as $\Delta H^{M}/\chi_{Ca(NO_3)_2}$ as a function of $\chi_{Ca(NO_3)_2}$. The limiting value of $\Delta H^{M}/\chi_{Ca(NO_3)_2}$ at $\chi_{Ca(NO_3)_2} = 1$ represents the heat of fusion of calcium nitrate at 623 K since, with no alkali metal nitrate present, no dissolution is involved, only the change of state from solid to supercooled liquid. Extrapolation of the results from each of the four binary systems to $\chi_{Ca(NO_3)_2} = 1$ gave a limiting value of 5.7 kcal mole^{-1}.

Equation (4) can be rewritten as

$$\Delta H_{M} = \chi_{Ca(NO_3)_2}\left(\frac{\Delta H^{M}}{\chi_{Ca(NO_3)_2}}\right) - \chi_{Ca(NO_3)_2}\,\Delta H_{F,Ca(NO_3)_2} \tag{5}$$

Thus ΔH_{M} can be calculated for any composition in any of the systems by putting $\Delta H_{F,Ca(NO_3)_2}$ equal to 5.7 kcal mole^{-1} and inserting the appropriate value of $\Delta H^{M}/\chi_{Ca(NO_3)_2}$ at $\chi_{Ca(NO_3)_2}$ as read from Kleppa's plots. For the $NaNO_3$—$Ca(NO_3)_2$ system, at $\chi_{Ca(NO_3)_2} = 0.299$

$$\frac{\Delta H^{M}_{(Na-Ca)}}{0.299} = 4.95 \text{ kcal mole}^{-1}$$

and

$$\Delta H_{M(Na-Ca)} = -0.22 \text{ kcal mole}^{-1}$$

For the KNO_3—$Ca(NO_3)_2$ system, at $\chi_{Ca(NO_3)_2} = 0.333$

$$\frac{\Delta H^{M}_{(K-Ca)}}{0.333} = 3.90 \text{ kcal mole}^{-1}$$

and

$$\Delta H_{M(K-Ca)} = -0.60 \text{ kcal mole}^{-1}$$

A direct comparison with our results is not possible, because we do not know the enthalpy of supercooled liquid $Ca(NO_3)_2$ and, hence, we cannot calculate ΔH_{M}. Writing eqn. (3) so that it applies to our systems at 623 K, the temperature of Kleppa's experiments and a temperature to which our results can reasonably be extrapolated, we obtain

$$\Delta H_{M} = (H_{623} - H_{298})_{sol,liq} - \chi_{(Na,K)NO_3}(H_{623} - H_{298})^{*}_{(Na,K)NO_3,liq} - \chi_{Ca(NO_3)_2}(H_{623} - H_{298})_{Ca(NO_3)_2,\text{ supercooled liq}} \tag{6}$$

Substituting $(H_{623} - H_{298})$ by Δh_{623} in all cases, using the values for $NaNO_3$ and KNO_3 from our earlier work [4], and inserting $\Delta H_{M(Na-Ca)}$ and $\Delta H_{M(K-Ca)}$ as calculated above, we obtain

$$-0.22 = \Delta h_{623(\mathrm{Na-Ca})} - 0.701 \times 14.91 - 0.299\ \Delta h_{623(\mathrm{Ca(NO_3)_2,\ supercooled\,liq})} \tag{7}$$

for the 0.701 $NaNO_3 \cdot 0.299\ Ca(NO_3)_2$ solution and

$$-0.60 = \Delta h_{623(\mathrm{K-Ca})} - 0.667 \times 13.11 - 0.333\ \Delta h_{623(\mathrm{Ca(NO_3)_2,supercooled\,liq})} \tag{8}$$

for the 0.667 $KNO_3 \cdot 0.333\ Ca(NO_3)_2$ solution. By combining these two equations, the calcium nitrate enthalpy term can be eliminated, resulting in an expression relating the magnitudes of the enthalpies of the two solutions

$$\frac{\Delta h_{623(\mathrm{Na-Ca})}}{0.299} - \frac{\Delta h_{623(\mathrm{K-Ca})}}{0.333} = 9.76$$

Inserting our experimental value for one of the enthalpies enables the calculation of the other, and hence the relative values of the two enthalpies. Putting $\Delta h_{623(\mathrm{Na-Ca})}$ equal to 15.45 kcal mole^{-1} [from an extrapolation of eqn. (1)] gives a value of 14.0 kcal mole^{-1} for $\Delta h_{623(\mathrm{K-Ca})}$, compared with the experimental value of 14.29 kcal mole^{-1} [eqn. (2)], and $\Delta h_{623(\mathrm{Na-Ca})}/\Delta h_{623(\mathrm{K-Ca})}$ equal to 1.10, compared with 1.08 when both values are the directly determined experimental values. Thus it seems that our work is in good general agreement with that of Kleppa.

In view of this, we have proceeded one step further and calculated the enthalpy of supercooled $Ca(NO_3)_2$ at 623 K by inserting our experimentally measured $\Delta h_{623(\mathrm{Na-Ca})}$ and $\Delta h_{623(\mathrm{K-Ca})}$ in eqns. (7) and (8), respectively. Equation (7) gives $\Delta h_{623(\mathrm{Ca(NO_3)_2,supercooled\ liq})}$ equal to 17.5 kcal mole^{-1}, while eqn. (8) gives 18.5 kcal mole^{-1}. The average of 18.0 kcal mole^{-1}, in conjuction with Kleppa's heat of fusion of 5.7 kcal mole^{-1} at the same temperature could be useful in estimating enthalpies and heats of fusion of other calcium nitrate containing solutions, there being a dearth of data for $Ca(NO_3)_2$.

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