THERMOPHYSICAL PROPERTIES OF MIXED ALKALI AND EARTH ALKALINE NITRATE SALTS USED AS HEAT TRANSFER FLUIDS FOR CONCENTRATED SOLAR POWER

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Introduction

Concentrated solar power (CSP) is a proven technology for the generation of electricity.[1] Currently, one of the biggest challenges limiting the competitiveness of CSP with traditional fossil fuel and nuclear energy sources is the intermittency of delivering electricity. Thermal energy storage is one potential solution to this challenge. The storage of heat, either in the form of sensible heat or latent heat, enables CSP plants to provide dispatchable and baseload electrical power. Our research developing new heat transfer fluids (HTFs) and thermal energy storage materials is directly aligned with improving the overall efficiencies of CSP plants by increasing the operating temperature and reducing the costs associated with thermal energy storage (TES).

Prior work has focused on low melting HTFs based on nitrate and nitrite salts.[2-4] Now, we are expanding our work to include the discovery of high temperature HTF fluids. The major benefit of increasing the upper operating temperature of CSP plants is better efficiency. Current HTFs based on synthetic oils or nitrate-based molten salts are limited to approximately 400 or 550 °C, respectively. With the discovery of higher temperature fluids, also comes the additional task of obtaining a full understanding of the thermophysical properties. From a systems analysis point-of-view, HTF properties like heat capacity, thermal conductivity, and heat of fusion should all be known for accurate costs estimations and 30-year plant lifetime designs. For individual components, thermophysical properties are well known over a wide temperature range. However, if a HTF is composed of mixtures of fluids, particularly molten salts, it is unclear whether or not these fluids will behave as ideal mixtures. Also of concern at temperature > 550 °C is the thermal stability of HTFs. Distinguishing between thermodynamic and kinetic stability, and developing a reliable experimental method remains elusive.

The focus of this work is twofold. First, do mixtures of molten salts behave as ideal liquids? We have measured the heat of fusion and heat capacity for mixtures of simple nitrate salts to determine whether or not they behave as idea mixtures.[5] Second, how does one define the thermal stability of a HTF? Preliminary kinetic experiments using TGA are presented.[6] Our method is compared to prior experimental work and expands the temperature range to coincide with current DOE targets set forth by the SunShot Initiative.

Experimental Section

Salts were purchased from commercial sources; $NaNO_3$ (Riedel-de-Haen), $NaNO_2$ (Sigma-Aldrich), $LiNO_3$ (Ricca Chemical), KNO_3 (Fisher Scientific), KNO_2 (Acros), $Ca(NO_3)_2 \cdot 4H_2O$ (Acros). Prior to use, salts were dried in an oven at 250 °C under a flow of nitrogen gas except for calcium nitrate, which was used as-received. The weight percent of water present in the hydrated calcium nitrate was calculated using a Mettler-Toledo Thermal Gravimetric Analysis Instrument (TGA/DSC 1) which, according to the observed mass loss, had 4.67 (±0.19) equivalents of water. Salt mixtures were

formulated with the desired composition using the anhydrous alkali nitrates and hydrated calcium nitrate. To ensure molecular mixing, samples (approximately 1 – 2 g) were dissolved in approximately 5 mL of deionized water in a 20-mL scintillation vial. The water was then evaporated in an oven at 80 °C with a nitrogen purge. Finally, the oven temperature was raised to 250 °C to remove all water. TGA-MS (50 – 600 °C) was used to confirm that no water remained in the binary salts. Anhydrous samples were ground into a fine powder and stored inside an argon-filled glove box. Samples for DSC measurements (10 – 30 mg) were prepared in hermetically sealed aluminum pans (40 μL). The pan lid was pierced immediately before acquiring data. A Mettler-Toledo DSC 823e equipped with an auto-sampler, was used for measuring heat capacity (Cp) and enthalpy (ΔH). The DSC was calibrated using In and Zn standards. A heating rate of 10 °C/min was used to measure the latent heat of melting. Heat capacities of both solid and liquid samples were determined using a proprietary method developed by Mettler-Toledo called TOPEM[7], These results were compared to the ASME sapphire method.[8] At least three measurements on different samples were performed and averaged to determine the reproducibility of data.

Results and Discussion

Are simple binary mixtures of molten salts ideal solutions in which the heat of fusion is proportional to the molar percentage of each constituent? To answer this question, the apparent heat of fusion for a series of mixed alkali/calcium nitrate salts was measured using differential scanning calorimetry (DSC). The data for three series of salt mixtures are plotted in figure 1 spanning 0 – 90 mol% calcium nitrate. Along the ordinate the heat of fusion for pure lithium, sodium and potassium nitrate are plotted and agree well with the reported values. As calcium nitrate is added, the apparent heat of fusion decreases significantly for an endothermic peak near 240 °C. Convergence at 2 kJ/mol is observed but this value is not the heat of formation for calcium nitrate.
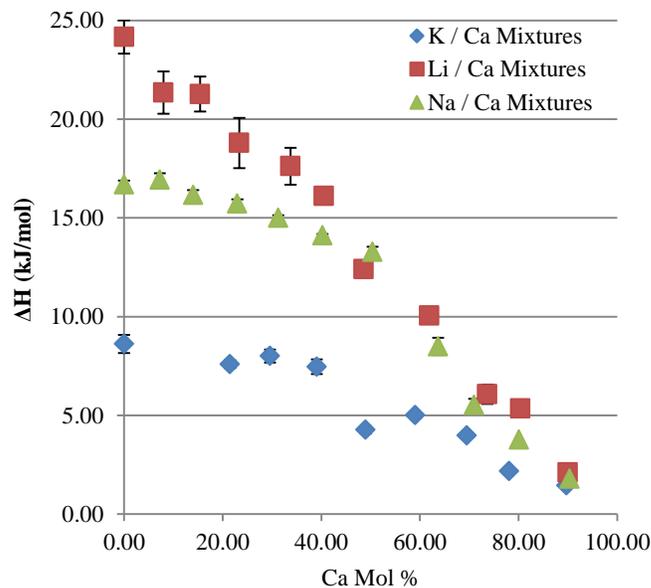
Fig. 1: Apparent heat of melting for three calcium/alkali nitrate mixtures.

Further DSC experiments up to 500 °C revealed a second heat flow not included in the data presented in Figure 1. These new data show that the apparent heat of melting is not simply proportional to the molar percentages of each constituent since off-eutectic phase-

changes occur. The apparent heat of melting plotted in figure 1 is only representative of the eutectic mixture melting below 300 °C. Visual inspection of mixtures (10 g-samples) revealed that even above 300 °C, in calcium-rich samples, a solid-phase remained. The convergence towards 2 kJ/mol as the mol% of calcium is increased, is therefore attributed to a decrease in the amount of material undergoing the solid-liquid transition of the eutectic below 300 °C.

Maeso and Largo investigated the liquid behavior of Li/Na and Li/K nitrate mixtures and calculated the activity coefficients and excess Gibbs Free Energy (G^E).[9] Two models were used to reproduce the experimental phase-diagrams determined by DSC. In a simplified fashion, the data collected here can be analyzed and used to calculated G^E. Table 1 gives the measured and predicted heat of fusion for Na/K, Li/K and Li/Na nitrate mixtures near the eutectic compositions determined in this work. The predicted heat of fusion assumes ideal mixing of the two binary mixtures at the eutectic point. In other words, ΔH is proportional to the molar percentage of each constituent. The average difference between the measured and predicted ΔH_{fus} is 2.75 kJ/mol.

Table 1. Comparison of measured and ideal ΔH_{fus} for alkali nitrate eutectic mixtures.

Cation	mol % Na	mol % K	[1]Measured ΔH_{fus}	[1,2]Predicted ΔH_{fus}
Na/K	49.71	50.29	9.11	13.00
	mol % Li	mol % K		
Li/K	39.76	60.24	13.33	15.23
	mol % Li	mol % Na		
Li/Na	50.97	49.03	18.04	20.50
[1] given in kJ/mol [2] based on the molar percentage of each pure component				

In a similar approach, ΔH_{fus} for calcium nitrate can be estimated from the eutectic Li/Ca and Na/Ca mixtures. In this treatment it is assumed that the measured heat of fusion for these binary mixtures is proportional to the molar percentage of each constituent plus G^E. Table 2 lists the measured ΔH_{fus} for both binary eutectic mixtures and the calculated ΔH_{fus} for $Ca(NO_3)_2$ assuming $G^E = 2.75$ kJ/mol. The two calculated values for ΔH_{fus} in table 2 derived from the Li/Ca or Na/Ca eutectic mixtures are within 0.3 kJ/mol of one another. A heat of fusion for pure $Ca(NO_3)_2$ at the eutectic melting temperature is calculated to be approximately 7.3 kJ/mol.

Table 2. Measured ΔH_{fus} for alkali/Calcium nitrate eutectic mixtures.

Cation	mol % Li	mol % Ca	[1] Measured ΔH_{fus} (kJ/mol)	[1,2]Calculated ΔH_{fus} for pure $Ca(NO_3)_2$ (kJ/mol)
Li/Ca	76.7	23.3	18.80	7.14 (240 °C)
	mol % Na	mol % Ca		
Na/Ca	68.7	31.3	15.00	7.44 (228 °C)
[1] given in kJ/mol [2] calculated at the eutectic temperature				

Conclusions

Simple binary mixtures of alkali and earth alkaline nitrate salts were investigated using differential calorimetry. Non-ideal mixing behavior was observed for all mixtures. A simplified correction factor, dedicated to the excess Gibbs' Free Energy, was determined for eutectic mixtures of binary alkali nitrates with known ΔH_{fus}. Next, the apparent heat of fusion for near-eutectic mixtures of Li/Ca and Na/Ca nitrates was measured. Since ΔH_{fus} for $LiNO_3$ and $NaNO_3$ are known, the heat of fusion for pure $Ca(NO_3)_2$ could be approximated using the measured apparent heat of fusion for the mixtures. A correction was used to account for the excess Gibbs' Free Energy. From these measurements, the heat of fusion for pure $Ca(NO_3)_2$ at the eutectic solid-liquid equilibrium temperature is estimated to be 7.3 kJ/mol.

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