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THERMOPHYSICAL PROPERTY ESTIMATIONS
OF MOLTEN SALTS

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Abstract

Projection of molten salt performance in thermal storage systems, whether based on sensible heat or latent heat, is highly dependent on the predictions of thermophysical properties. In the absence of experimental data, heat transfer properties rely on theoretical estimations. This work focuses on thermodynamic predictions of mixture properties for molten salts supportive of ongoing advanced heat transfer fluid research at the Sandia National Laboratories. Thus far, the candidate mixtures studied experimentally and theoretically at Sandia are made up of either ternary or quaternary nitrate and mixed nitrate/nitrite salts of various compositions. Experimentally, mixture properties such as melting points and heat of fusion are obtained by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Classical thermodynamics are applied to resolve phase transitions of molten salt mixtures as well as mixture properties. The Wilson equation, developed originally for organic mixtures, is used to study phase boundaries of molten salts in this work. Molecular thermodynamics (MD), where atomistic simulation forms the basis for constructing the equation of state, are conducted where our fundamental understanding and experimental knowledge are lacking.

Introduction

Molten salts have been identified as a suitable class of working fluids for concentrated solar power systems. While achieving higher efficiencies for heat storage relative to organic heat transfer fluids, they are limited by high melting points and thermal stability. Numerous past experiments have focused around measurements of heat transfer properties, such as heat capacity and thermal conductivity. However, seeking potential candidates by experimentation is a challenging and expensive endeavor. When the number of components in a molten salt mixture increases, one must rely on predictive methods to expedite searches for thermophysical properties that exhibit desired heat transfer characteristics.

Sandia National Laboratories have conducted experiments and simulations to explore properties of molten salt mixtures, mostly centered around phase transition studies. The candidates that have been studied experimentally are made up of either ternary or quaternary nitrate and mixed nitrate/nitrite salts of various compositions [1,2]. Just to map out melting points of these mixtures across combinatorial composition-temperature-pressure space would be a time-consuming and expensive endeavor by experimentation alone.

This study describes the progress achieved thus far, and the continuing pursuit of harmonizing past and current efforts towards better design of heat transfer materials.

Melting Point Studies

Combined experimental and modeling studies explore solid-liquid transition nitrate and nitrate/nitrite mixtures. In particular, the study aims to deduce the eutectic composition where the transition from solid to liquid is at the lowest temperature point. The numerical studies of the phase equilibria of nitrate salts were based on classical thermodynamics to develop a rapid modeling capability to reduce the breadth of experimental mixtures studies required. The theory is derived from Prausnitz et al. and relates the free energy change of the solid-liquid phase transition to the ratio of fugacities and the activity coefficient as shown below [3]:

$$ln\frac{1}{\gamma_i x_i}=\frac{\Delta_{\mathrm{fus}}\mathrm{h_i}}{RT_m}\left(\frac{T_m}{T}-1\right).$$

Where γ_i is the activity coefficient, x_i is the solubility, $\Delta_{fus}h_i$ is the heat of fusion, R is the universal gas constant, T_m is the melting temperature, and T is the mixture temperature. The Wilson equation is used to calculate the activity coefficients for each component in the mixture [4]. The Wilson equation to calculate the activity coefficient of component k of m components is

$$ln\gamma_k=-ln\left(\sum_{j=1}^{m}x_j\Lambda_{\mathrm{kj}}\right)+1-\sum_{i=1}^{m}\left(\frac{x_i\Lambda_{ik}}{\sum_{j=1}^{m}x_j\Lambda_{ij}}\right).$$

In the Wilson equation Λ_{ij} and Λ_{ji} are defined as the interaction coefficients of *i-j* and *j-i* pairs. The interaction coefficients are used as fitting parameters in order to fit the numerical predictions of binary mixtures to experimental results of the phase equilibria. Using the binary interaction coefficients, the Wilson equation is extended to predict the phase equilibria of mixtures of three and four components. One goal of the study was to find mixtures of nitrate salts with the lowest melting point. When combining three salts, the lowest melting point is a combination of 37% (by mole) $LiNO_3$, 36% KNO_3, and 27% $CsNO_3$ which melted at 115°C. With four salts a mixture of 28% (by mole) $LiNO_3$, 14% $NaNO_3$, 33% KNO_3, and 25% $CsNO_3$ is predicted to melt at 100°C. Figure 1 illustrates an example of quaternary phase diagram for mixture of lithium nitrate, potassium nitrate, sodium nitrate, and cesium nitrate [5].

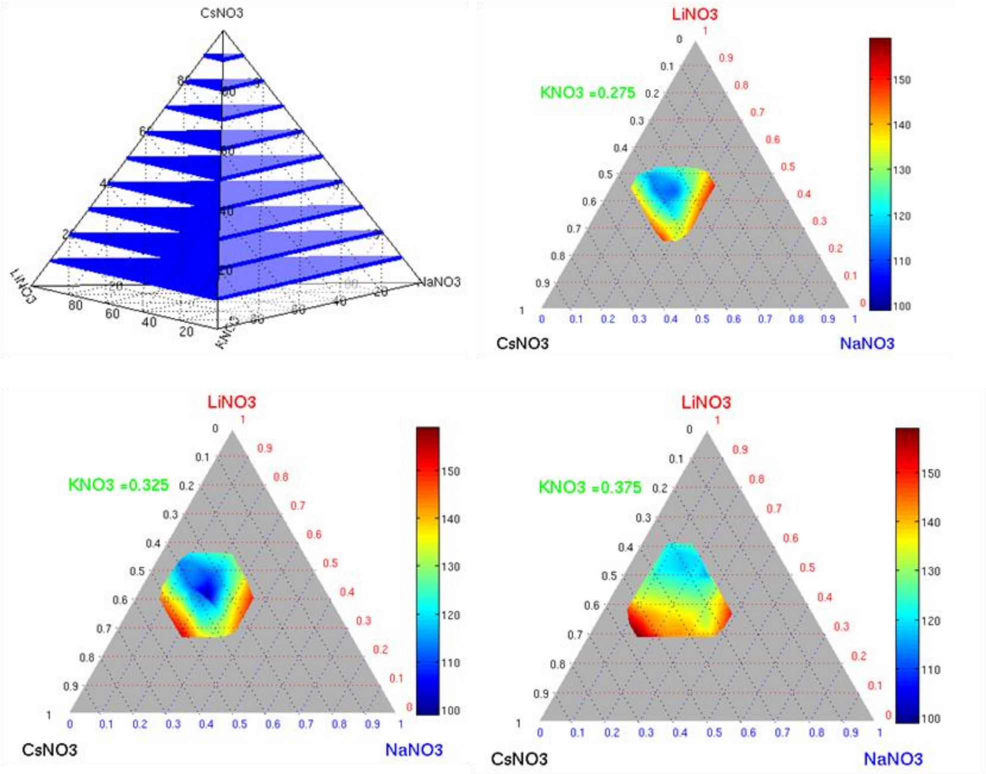

Figure 1 Quaternary phase diagram of lithium nitrate ($LiNO_3$), sodium nitrate ($NaNO_3$), potassium nitrate (KNO_3), and cesium nitrate ($CsNO_3$).

Experimentally, the effect of adding nitrite to the mixture is illustrated in Figure 2, where the melting point is plotted against the concentration of nitrate anion. Increasing lithium cation concentration lowers the melting temperature until it passes 34%-35%. Beyond that concentration, the melting point becomes insensitive to lithium cation. The melting point also decreases with increasing concentration of nitrate ion. The correlation to nitrate ion appears to be linear.

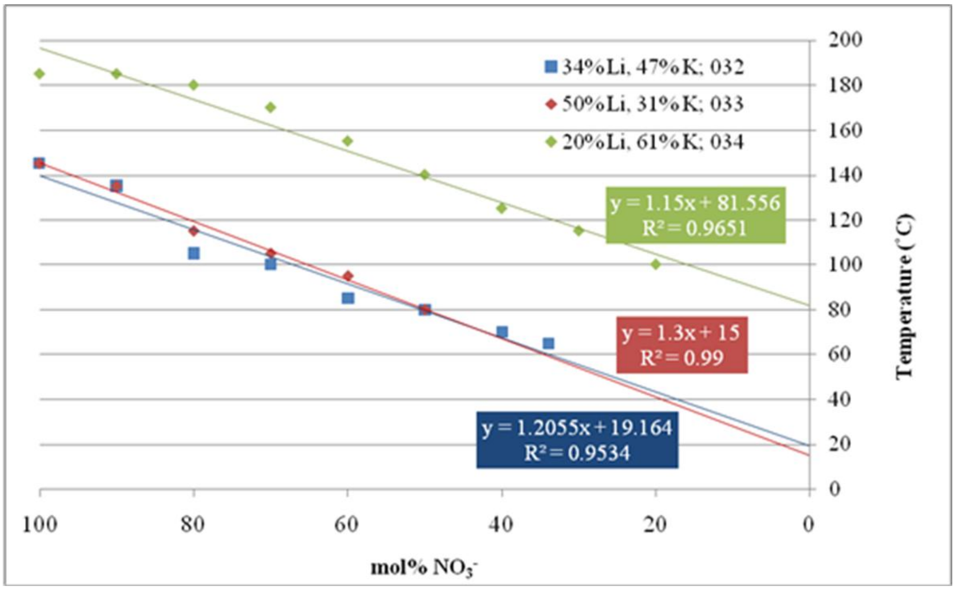

Figure 2 – Melting temperature data for mixtures of lithium nitrate ($LiNO_3$), potassium nitrate (KNO_3), sodium nitrate ($NaNO_3$), sodium nitrite ($NaNO_2$), and potassium nitrite (KNO_2), at various concentrations of lithium cation and nitrate anion.

Heat of Fusion

Similar to the melting point studies, experimental and theoretical effort are conducted to analyze pure component thermophysical properties. Constant temperature molecular dynamics simulations were conducted on the solid and liquid phases and the enthalpies of the solid and liquid phases were computed. The enthalpy difference between solid and liquid phases for pure component calcium nitrate $Ca(NO_3)_2$ is plotted as a function of temperature in Figure 3. The experimentally measured enthalpy of fusion is higher than the theoretical value predicted from Figure 3 at the experimental melting point of pure $Ca(NO_3)_2$. The theoretical value underestimates the enthalpy of fusion due to insufficiencies in the interatomic potential used [6]. Notwithstanding inaccuracies, these simulations offer valuable tools to estimate pure-component properties that are either difficult to measure or are non-existent.

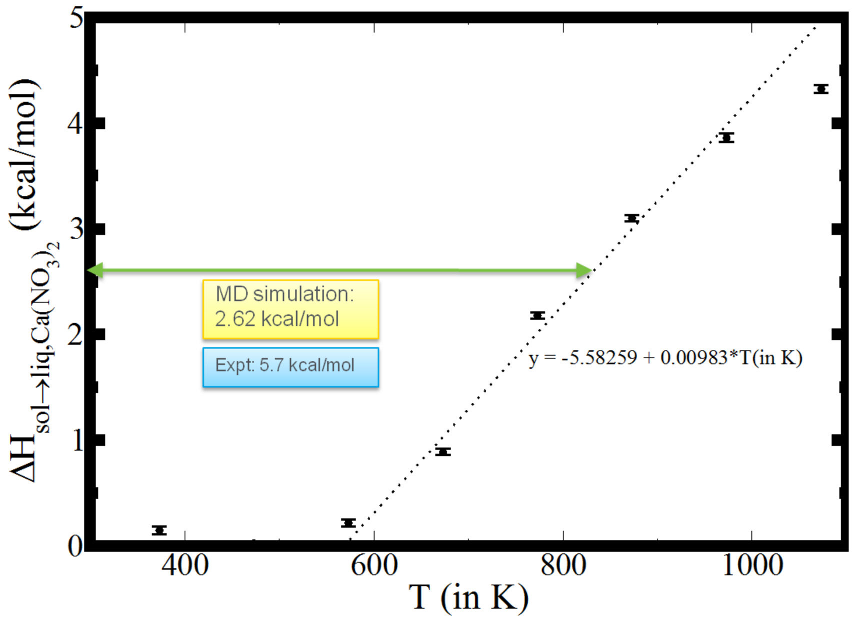

Figure 3 –Enthalpy between pure solid and pure liquid calcium nitrate as a function of temperature.

The heat of fusion is also measured experimentally for different binary mixtures. Figure 4 shows experimental data for Na/Ca nitrate mixtures. As the mol% of calcium increases, the apparent heat of melting decreases. Because pure calcium nitrate cannot be melted without undergoing decomposition, measuring the apparent heat of fusion for mixtures may enable us to extrapolate to 100% calcium nitrate. Binary salt mixtures based on lithium and potassium have also been investigated. These data, when looked at together, allow us to understand mixing behavior of salts and potentially predict thermodynamic properties based on classical models.

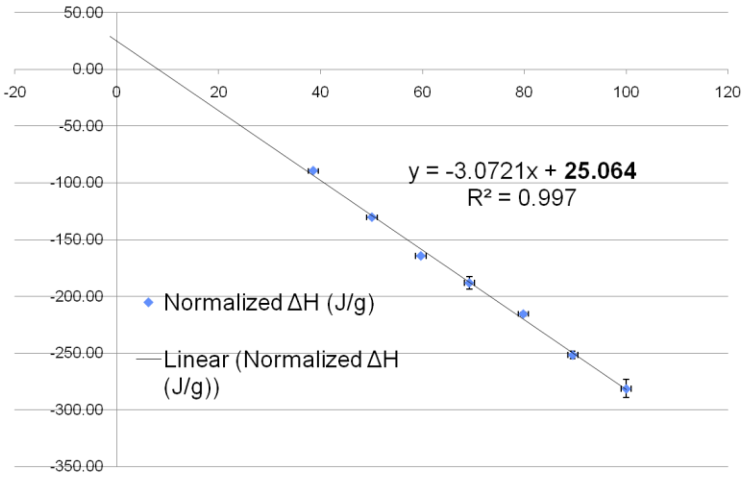

Figure 4 – Heat of fusion from solid to liquid for binary lithium nitrate/sodium nitrite mixture. The x-axis represents percentage of lithium nitrate.

Harmonization Study

There are numerous concurrent effort investigating candidate fluids that offer desirable heat transfer performance. Historical experiments that focused on discovery of thermal storage media collected over the years are also revisited to understand the variability of thermophysical properties. Figure 5 illustrates just a few examples of the relationship between melting points and thermal energy density. Table 1 summarizes the historical reports used to generate the data.

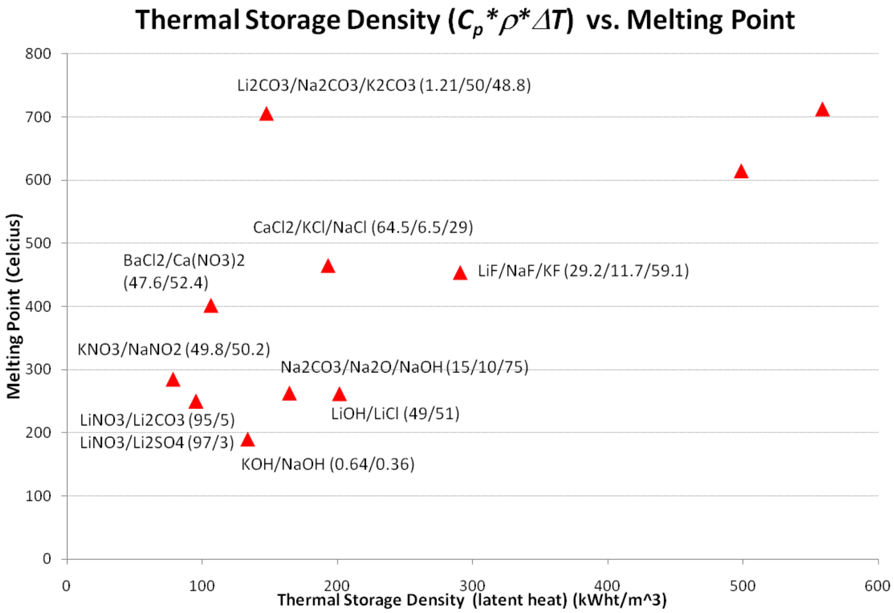

Figure 5 – Plot of melting points of various inorganic salt mixtures versus thermal storage density, defined as the product of liquid heat capacity, liquid density, and working temperature range. References are given in Table 1.

Concurrently, Halotecnics is using a proprietary high-throughput method to systematically screen combinatorial mixtures of molten salt [7]. Concurrent to this DOE-funded effort, similar experimental studies are underway at the University of Alabama and University of Wisconsin [8].

Summary

This work summarizes the effort towards understanding of molten salts heat transfer characteristics conducted at Sandia. Theoretical and experimental efforts are conducted internally to support the National Solar Thermal Testing Facility (NSTTF). Molecular dynamics and classical thermodynamics are both used to elucidate pure component as well as high-order mixture phase transition properties. Experiments are also conducted to explore novel mixtures that yield best heat transfer characteristics.

Acknowledgement

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Table 1 – References for Figure 5.

Author(s)	Title	Date	Publisher	ID
Ferrara, Angelo, George Yenetchi, Robert Haslett, Robert Kosson	Thermal Energy Storage Heat Transfer	Oct-77	NASA	NASA CR 135244
Ferrara, Angelo	Thermal Energy Storage Heat Exchanger	Sep-77	ORNL	CONF-770955
Haslett, R., J. Alario, and G. Yenetchi	Active Heat Exchanger System Development for Latent Heat Thermal Energy Storage System	Dec-78	SNL/CA	CONF-781231
LeFrois, R.T., G.R. Knowles, A.K. Mathur, and J. Budimir	Active Heat Exchange System Development for Latent Heat Thermal Energy Storage	Feb-79	Honeywell/NASA/DOE	DOE/NASA/0038-79/1
Alario, Joseph, Robert Kosson, and Robert Haslett	Active Heat Exchange System Development for Latent Heat Thermal Energy Storage	Jan-80	Grumman/NASA/DOE	DOE/NASA/0039-79/1
Petri, Randy.J., Terry D. Claar, and Estela T. Ong	High-Temperature Molten Salt Thermal Energy Storage Systems for Solar Applications	Jul-83	IGT/NASA/DOE	DOE/NASA/0156-83/1
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