

THERMODYNAMIC PROPERTIES OF MOLTEN NITRATE SALTS

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Abstract

Molten salts are being employed throughout the world as heat transfer fluids and phase change materials for concentrated solar power (CSP) production and storage. In order to design large production facilities, accurate physical and thermodynamic properties of molten salts must be known. Required data include a) melting point; b) viscosity; c) apparent heat of fusion; d) thermal conductivity; e) heat capacity; f) density; g) volumetric expansion; and h) vapor pressure. Data are available for many pure components which make up molten salt mixtures. However, there are some missing or inconsistent numbers in the literature, especially for materials at elevated temperatures. This paper summarizes our most current thermodynamic measurements for some pure salts and mixtures which are of interest as heat transfer fluids and phase change materials (PCM). Specifically, data on the apparent heat of fusion (ΔH_{fus}) and heat capacity (C_p) for a family of nitrate and nitrite salts are reported. These data are critical for estimating costs associated with parabolic trough systems, central receiver towers, and thermal storage tanks.

Keywords: Nitrate, Molten Salts, Heat Capacity, heat of Fusion

1. Introduction

Our current work focuses on expanding the database of thermophysical properties of alkali and alkaline earth cations with nitrate or nitrite anions. Previous reports from our group discuss low-melting salts containing lithium, sodium, potassium and calcium cations with nitrate and nitrite anions. [1, 2] Among other things, we reported liquidus temperatures, densities, and viscosities. While some properties can be modeled reasonably accurately assuming ideal mixing behavior (e.g. density), other properties (e.g. viscosity) show non-ideal mixing behavior. This paper investigates the assumption that changes in latent heat of fusion and heat capacity for a series of nitrate and nitrite salts follow ideal mixing behavior; i.e. that the apparent heat of melting and heat capacity of binary mixtures will be proportional to the mole fraction of the pure components. Ultimately, the goal of this research is collect enough data so that accurate extrapolations and predictive models can be developed for explorative screening of new materials.

Calcium nitrate, or $\text{Ca}(\text{NO}_3)_2$, is of interest for use as a heat transfer fluid and phase-change material because it is inexpensive, depresses the melting point, and can improve the thermal stability of mixed-molten salts. [1] However, no direct measurement of the enthalpy of fusion (ΔH_{fus}) has been reported in the literature, presumably because calcium nitrate decomposes upon melting. In 1961, Kleppa and Hersh reported heats of mixing data for a series of alkali and calcium nitrate salts obtained using a micro-calorimeter. In their work, molten alkali nitrate at 350 °C was used to dissolve known amounts of anhydrous calcium nitrate. These solid-liquid mixing experiments were used to extrapolate the heat of fusion for pure calcium nitrate at 350 °C as 24 kJ/mol. [3] The true melting point of calcium nitrate is 561 °C and Kleppa and Hersh go on to mention that the heat of fusion for calcium nitrate “probably increases substantially with increasing temperature”. In this work, we use differential scanning calorimetry (DSC) to measure the apparent heat of fusion (ΔH_{fus}) for a series of alkali and calcium nitrate salts. We wish to test the assumption that simple binary mixtures are ideal solutions by determining if the heat of fusion is proportional to the molar percentage of each constituent. If binary mixtures are found to behave as ideal solutions, then extrapolation to pure calcium nitrate will be possible. For non-ideal mixtures, the deviation from linearity will be related to the heat of mixing. Similarly, by measuring the heat capacity of mixed alkali/calcium nitrate molten salts, it may be possible to estimate the heat capacity of pure calcium nitrate via extrapolation.

2. Experimental Section

Salts were purchased from commercial sources and are listed here: NaNO_3 (Riedel-de-Haen), NaNO_2 (Sigma-Aldrich), LiNO_3 (Ricca Chemical), KNO_3 (Fisher Scientific), KNO_2 (Acros), and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Acros). Prior to use, salts were dried in an oven at $250\text{ }^\circ\text{C}$ 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). According to the observed mass loss, the hydrated calcium nitrate contained 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 $80\text{ }^\circ\text{C}$ with a nitrogen purge. Finally, the oven temperature was raised to $250\text{ }^\circ\text{C}$ to remove all water. TGA-MS ($50\text{ -- }600\text{ }^\circ\text{C}$) 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 (C_p) and enthalpy (ΔH). The DSC was calibrated using In and Zn standards. A heating rate of $10\text{ }^\circ\text{C}/\text{min}$ 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 [4], which compares well with the ASME sapphire method. [5] At least three measurements on different samples were performed and averaged to determine the reproducibility of data.

3. Results and Discussion

3.1. Dehydration of Calcium Nitrate Tetrahydrate

The dehydration of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was re-investigated using a thermal gravimetric analysis (TGA) instrument with a built-in DSC sensor coupled to a mass spectrometer (MS). As reported by previous groups, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ melts between $38\text{ -- }44\text{ }^\circ\text{C}$ to give a clear liquid. [6, 7]. Water is lost above $60\text{ }^\circ\text{C}$ and continues to evolve until the sample is fully dried at $180\text{ }^\circ\text{C}$. [8] At $180\text{ }^\circ\text{C}$ in air, the anhydrous salt appears to be stable with respect to losing NO or O_2 to form calcium oxide; no change in the sample mass is observed by TGA and no volatile species are detected by mass spectroscopy. Furthermore, the DSC signal is flat during this isothermal stage. As the temperature is raised $10\text{ }^\circ\text{C}/\text{min}$, a sharp endothermic event occurs near $544\text{ }^\circ\text{C}$ with a measurable weight loss in the TGA. Ions with $m/z^+ = 30$ and 32 are detected via mass spectroscopy, which correspond to NO and O_2 . (Figure 1) These experiments show that $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ can be dried at $180\text{ }^\circ\text{C}$. However, because anhydrous calcium nitrate decomposes upon melting above $544\text{ }^\circ\text{C}$, the enthalpy of fusion cannot be directly measured. Similarly, the heat capacity of molten calcium nitrate cannot be determined directly since the salt decomposes upon melting.

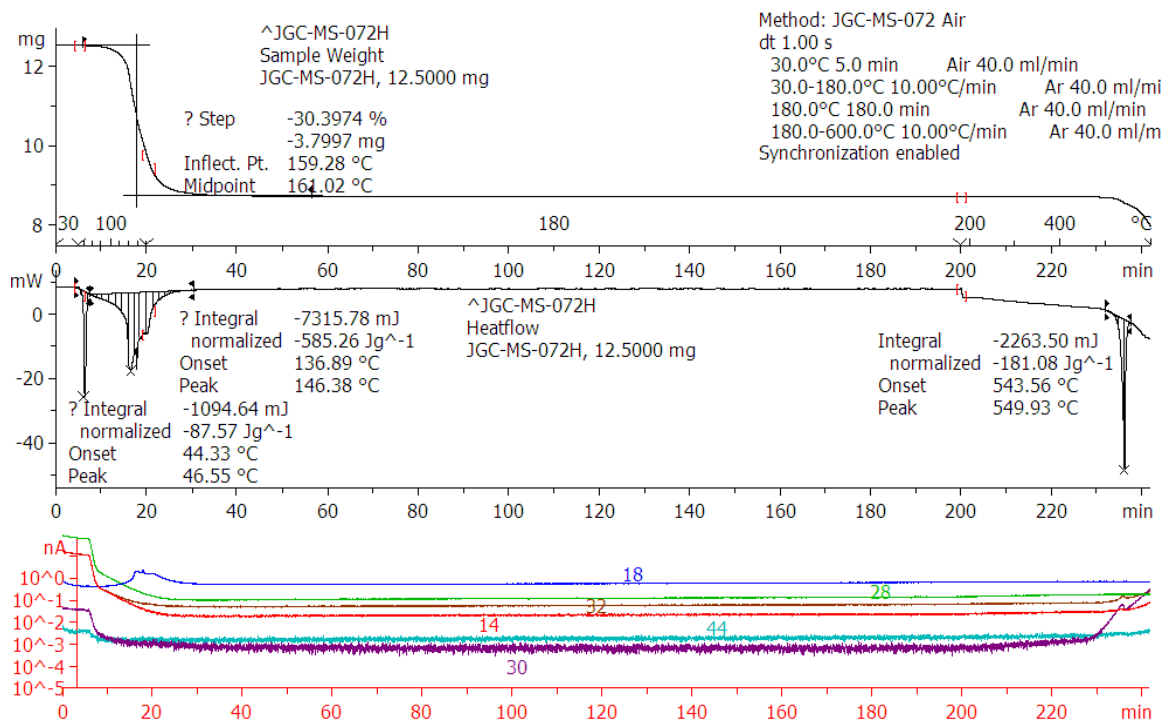


Figure 1: Thermal decomposition of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Top trace is TGA. Middle is DSC curve. Bottom traces are MS data, which show only $m/z^+ = 18$ (water) corresponding to initial weight loss in TGA until temperature > 544 °C, at which point NO and O_2 evolve.

3.2. Heat of Fusion Measurements

A series of nitrate salts were formulated using lithium (Li), sodium (Na), and potassium (K) mixed with calcium (Ca). The mole ratio of alkali cation/calcium cation varied between 100 – 35 mole percent. DSC was used to measure the apparent heat of melting for pure substances and all mixtures. The results of triplicate runs are plotted in Figure 2. The measured enthalpies are reported in kJ/mol using the principles of mole-fraction additivity and the molecular weight of the pure salt. The heat of fusion for pure salts (excluding calcium nitrate) can be found along the y-axis at 0 mol% Ca. Table 1 summarizes our experimental data for pure salts as well as literature data.

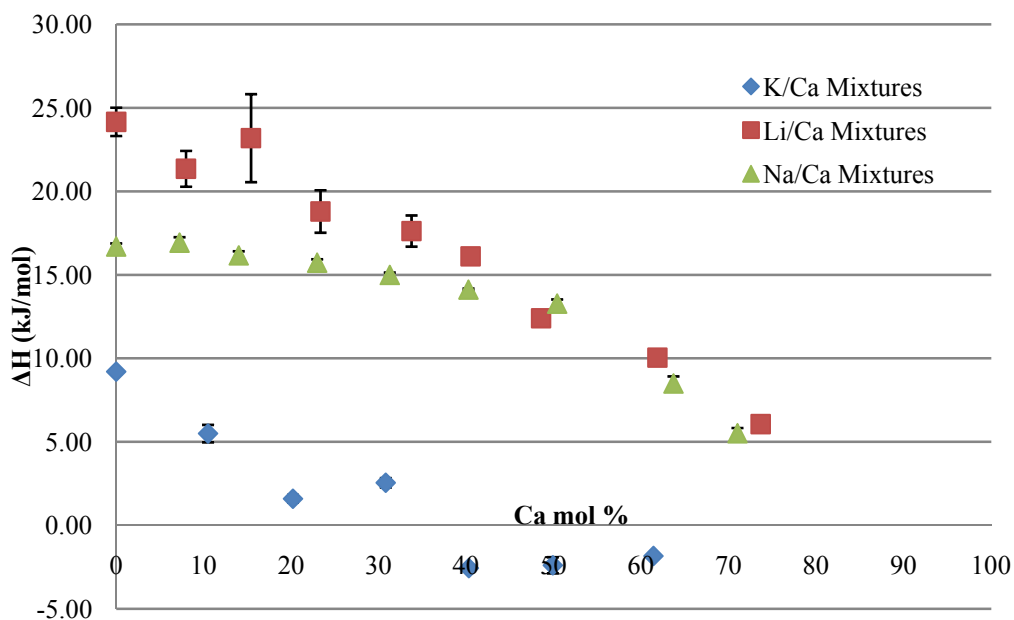


Figure 2: Apparent ΔH of melting (kJ/mol) for alkali/Ca nitrate mixtures plotted versus Ca mol%.

Salt	ΔH_{fusion} (this work)	Lit value (method) [ref]	Lit value (method) [ref]	Lit value (method) [ref]	Lit value (method) [ref]
LiNO ₃	24.32 (± 1.42)	25.03 (DSC) [9]	24.5 (DSC) [10]	-	-
NaNO ₃	16.79 (± 0.26)	14.74 (DSC) [11]	15.44 (DSC) [12]	14.73 (DSC) [13]	14.70 (DSC) [9]
KNO ₃	9.20 (± 0.36)	10.00 (DSC) [12]	9.77 (DSC) [9]		
Ca(NO ₃) ₂	0 – 5	23.85 (extrapolated micro-calorimetry) [3]	-	-	-
NaNO ₂	13.77 (± 0.39)	14.57 (DSC) [11]	13.97 (DSC) [14]	-	-
KNO ₂	9.85 (± 0.44)	-	-	-	-

Table 1: Compiled enthalpy data for nitrate and nitrite salts

Lithium nitrate has the highest heat of fusion with $\Delta H = 24.32 (\pm 1.42)$ kJ/mol. Sodium and potassium nitrate are somewhat lower with $\Delta H = 16.79 (\pm 0.26)$ and $9.20 (\pm 0.36)$ kJ/mol. The measured values found via DSC compare well with literature data (Table 1). Binary mixtures with calcium nitrate are plotted along the x-axis and show a decreasing apparent heat of fusion with added calcium. As is evident from Figure 2, none of these mixtures exhibit ideal-mixing behavior. Both the Li/Ca and Na/Ca samples appear to converge at higher calcium mol%. Interestingly, the apparent heat of melting approaches 5 kJ/mol above 70 mol% calcium. If these data are extrapolated to 100 mol% calcium, a *negative* heat of melting is expected for pure Ca(NO₃)₂. Such an observation is not inconsistent with the thermodynamic instability of calcium nitrate upon melting (vide supra).

3.2.1. Further Investigation of K / Ca Nitrate Mixtures

Binary K/Ca nitrate salt mixtures deviate the most from ideality in this series of salts. The DSC traces for these mixtures show multiple endothermic and exothermic heat flows as the sample temperature is raised from 50 – 500 °C. Shown in Figure 3 are the DSC traces of three different salt samples containing 61.4 mol% calcium cation. The average heat flow over this entire region is -1.83 kJ/mol with a standard deviation of 0.17. The near-zero heat flow and high reproducibility of the measurement suggests a meta-stable solid state glass.

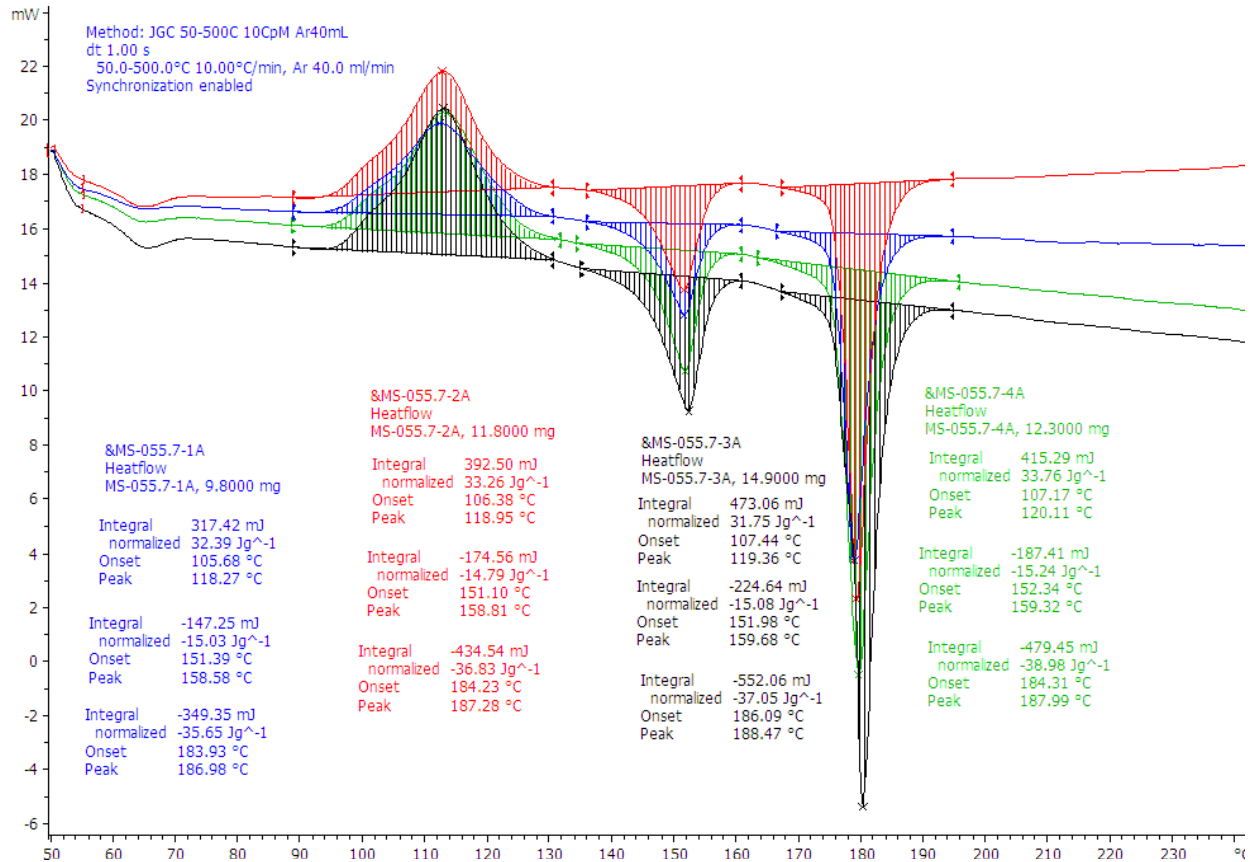


Figure 3: Three duplicate DSC traces of K/Ca nitrate salt with 61.4 mol% Ca.

In contrast to the Li/Ca or Na/Ca binary salts, which generally solidify as white powders, the solid K/Ca nitrate salts appear as hard, clear glasses. While only speculative, it appears that K/Ca nitrate mixtures form a solid-glass upon cooling—a well-documented phenomenon for certain calcium mixtures. [7] Excess strain in the meta-stable solid structure released as the sample temperature is raised could account for the early exothermic heat flow. While a thermodynamic model could potentially be used to describe the observed, non-ideal mixing behavior, such an approach is beyond the scope of this paper. It should be noted that the measured heat of melting for pure components does not include any solid-solid phase changes. However, the apparent heat of melting for the mixtures does include all observable enthalpy changes in the samples.

3.2.2. Observations of Other Nitrate Mixtures

Our mixing experiments were extended to Li/Na, Li/K, and Na/K nitrate and a binary nitrite salt. Samples with compositions ranging from 0 – 100 mol% of each constituent were analyzed via DSC. While the latent heat of melting for pure salts matched well with previous reports, mixtures were non-ideal. Off-eutectic behavior, evident by solid-solid phase changes or bimodal heat flows separated by up to 100 °C, was common for most samples and

can be seen in Figures 4 and 5. For example, the Li/K nitrate mixtures, which have been analyzed previously by Maeso and Largo showed non-ideal mixing with significant excess Gibbs energy of mixing. [10] A detailed analysis of the Gibbs energy of mixing and activity coefficients is beyond the scope of this paper.

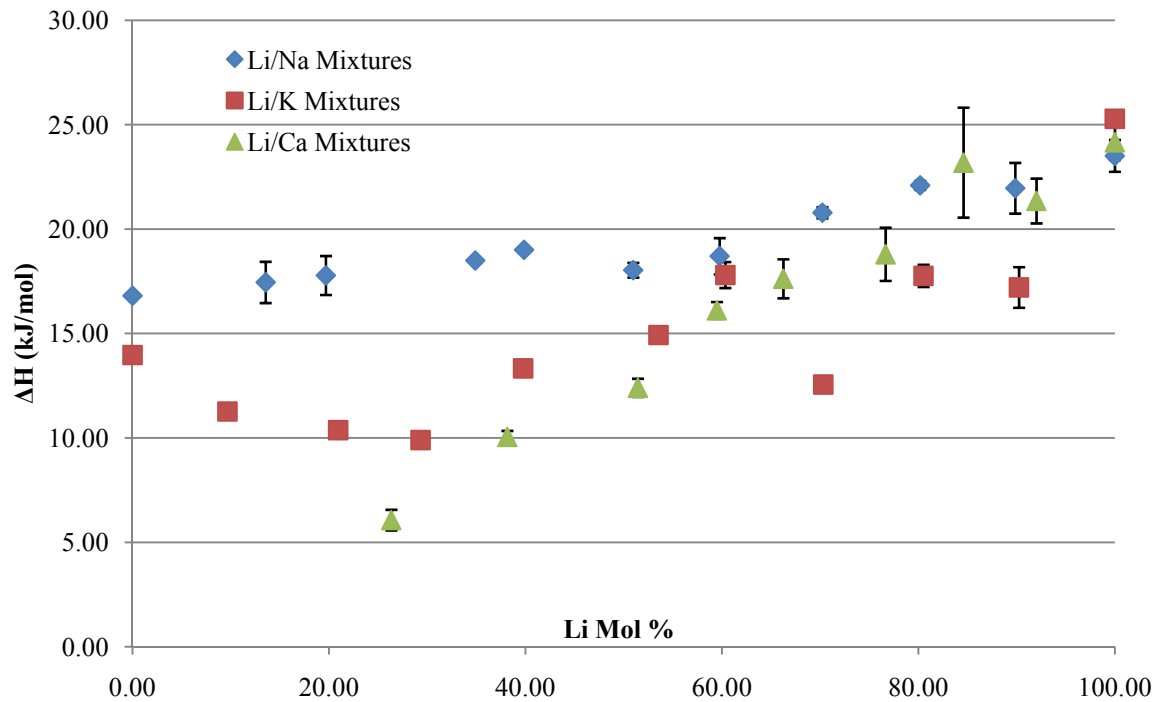


Figure 4: Apparent ΔH of melting (kJ/mol) for Li nitrate mixtures plotted versus Li mol%.

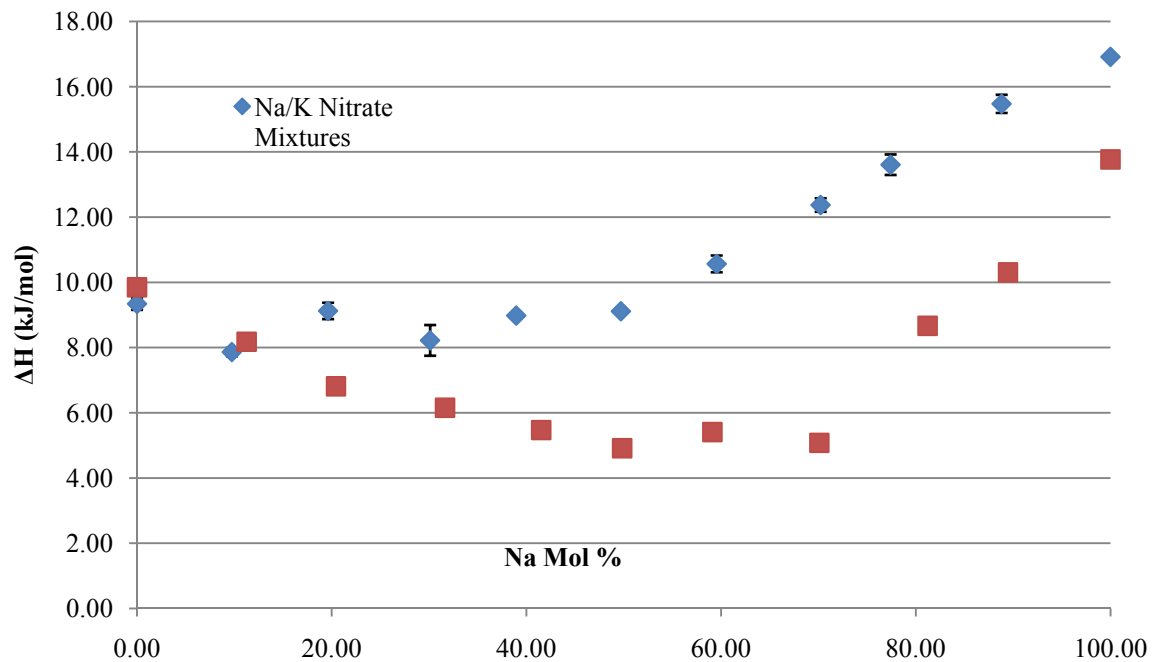


Figure 5: Apparent ΔH of melting (kJ/mol) for Na/K mixtures plotted versus Na mol%.

3.3. Heat Capacity Determination (C_p)

We used a temperature-modulated DSC method developed by Mettler-Toledo to measure the heat capacity of pure nitrate and nitrite salts plus eutectic mixtures. TOPEM® has been described in the literature and allows for direct measurement of both reversing and non-reversing heat flows.[4] The aim of these measurements was two-fold: to demonstrate that TOPEM® can be used to measure the heat capacities of pure nitrate salts and to determine the heat capacity of calcium nitrate by measuring the heat capacities of mixtures of alkali and calcium nitrate salts and then extrapolating to the pure salt. In order to make a simple linear extrapolation to 100 mol% calcium nitrate, it must be true that the salts analyzed by the TOPEM method are ideal mixtures. Part one of this report showed that none of the binary mixtures exhibited ideal mixing. The Li/Ca and Na/Ca nitrate salt mixtures did show convergence at higher calcium mol% but only an estimation of the latent heat of fusion could be made. Our heat capacity measurements therefore focus on these salt samples.

Table 2 summarizes the heat capacity data for three pure nitrate salts, literature data, and our approximation for the heat capacity of calcium nitrate. At this time, it is not possible to give an accurate prediction for the heat capacity of calcium nitrate. Binary mixtures gave irreproducible data so only a rough estimation is given. Preliminary results show that the heat capacity increases slightly with added calcium nitrate. Therefore, an approximate value for the heat capacity of pure calcium nitrate is 140 – 160 J/mol/K.

Salt	C_p (J/mol/K) (this work)	Lit value (method) [ref]	Lit value (method) [ref]	Lit value (method) [ref]
LiNO ₃	142.99 ± 1.68 (550-655K)	142.04 (535-650 K) (DSC) [9]		
NaNO ₃	140.58 ± 0.27 (590-655K)	142.72 ± 5.86 (580-700K) (DSC) [12]	130.54 (DSC) [13]	141.93 (585-650K) (DSC) [9]
KNO ₃	138.41 ± 1.10 (610-655K)	142.26 ± 7.11 (600-720K) (DSC)[12]	141.0 ± 1.3 (630-700K) (DSC)[15]	140.53 (615-730K) (DSC)[9]
Ca(NO ₃) ₂	140 - 160 (550 – 655 K)	-	-	-
NaNO ₂	110.48 ± 1.14 (625-675K)	117.67 ± 2.15 (570-670K) (DSC)[14]	116.7 ± 0.8 (571-630 K) (DSC)[15]	
KNO ₂	120.42 ± 1.43 (745-800 K)	-	-	-

Table 2: Compiled heat capacity data for nitrate and nitrite salts (J/mol/K)

4. Conclusion

The assumption that the enthalpy of mixing for alkali and earth alkaline nitrate/nitrite salts is additive is not valid. All binary mixtures investigated in this work showed non-ideal mixing, deviating from a linear prediction for entropy changes in fusion. It is evident that the apparent enthalpy of fusion decreases as more calcium is included and approaches zero or even negative enthalpy at 100 mol% calcium nitrate. The implication of this observation means phase-change storage systems based on calcium nitrate will have a significantly lower energy density compared to mixtures containing only alkali salts (Li, Na, K). The heat capacity of molten calcium nitrate is estimated to be roughly 120 – 140 J/mol/K, a value consistent with other alkali nitrate salts. The fundamental thermodynamic data collected by this research are being utilized to model ideal heat transfer fluids and storage systems for concentrated solar power facilities. The addition of calcium nitrate to any mixture of alkali nitrates causes a reduction in the latent heat and, hence, a reduction in the potential thermal energy storage capacity.

Acknowledgements

Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin company, for the United States Department of Energy under contract DE-AC04-94AL85000. SAND 2011-5576C.

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