



Experimental verification of theoretically estimated composition and enthalpy of fusion of eutectic salt mixtures



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ABSTRACT

The design of latent heat thermal energy storage systems is critically dependent on the properties of the chosen Phase Change Material (PCM). Currently published data on the thermodynamic properties of eutectic salts contains contradictory data, impeding the selection of PCMs.

In this work, previously elaborated theoretical methods for predicting the composition and enthalpy of fusion for eutectic salt mixtures is experimentally validated for three ternary eutectic mixtures: $\text{LiNO}_3 + \text{NaNO}_3 + \text{KNO}_3$, $\text{Li}_2\text{CO}_3 + \text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$, and $\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{Na}_2\text{SO}_4$. For each combination of salts, the eutectic composition suggested by published sources and the composition predicted by the theory are created. The latent heat of fusion, melting temperature, and congruency of the melting peak of these six mixtures are examined via differential scanning calorimetry. In addition, scanning electron microscopy and energy dispersive spectroscopy are used to verify the expected eutectic structure. Analysis of these six mixtures confirms that the composition can be predicted to within 8%. The enthalpy of fusion can be predicted to within 10% of experimental results. In addition, three binary eutectics ($\text{NaCl} + \text{Na}_2\text{SO}_4$, $\text{KCl} + \text{K}_2\text{CO}_3$, and $\text{NaCl} + \text{Na}_2\text{CO}_3$) are created and the theoretical enthalpy of fusion is experimentally verified.

1. Introduction

In order to reduce the total cost of Concentrated Solar Thermal Power, every sub-system must be optimized for cost. In particular, the Thermal Energy Storage (TES) system must be designed to reduce cost while still storing energy in the correct temperature range [1]. To achieve these goals, selecting the optimal storage medium is imperative. Prior research has investigated eutectic salt mixtures as storage media in Latent Heat Thermal Energy Storage Systems (LHTESS). As a subset of TES, LHTESS use the phase change of storage media to store energy in narrow temperature ranges with high volumetric energy density [2]. This increases the efficiency and cost effectiveness of TES systems. Eutectic salt mixtures are good candidates for storage media as there is a large possible combination space of mixtures, they have large latent heats, they are available in industrial quantities, and present excellent value. Thus, for every temperature range there are multiple possible mixtures [3]; from which the most cost effective option can be determined and selected for the application. Unfortunately, this selection often requires extensive and time consuming experimental testing.

The design of LHTESS are further complicated by published data on the storage media that are often contradictory. For example, two

reports for the latent heat of the salt eutectic $\text{NaCl} + \text{MgCl}_2$ [4,5], $430 \text{ J}(\text{g})^{-1}$ and $328 \text{ J}(\text{g})^{-1}$ respectively, contradict each other. Further testing of this eutectic yields $204 \text{ J}(\text{g})^{-1}$ [6]. Thus, the selection process is made difficult by the lack of reliable data for thermodynamic properties of the storage media. The impractical experimental task of blanket testing motivates the creation of a theoretical model which can accurately assess these thermodynamic properties.

In this study, a method for predicting the latent heat and a method for predicting the composition are experimentally verified. Additionally, the latent heat of several previously studied eutectics is experimentally verified to corroborate previous results in the literature. Experimental work was conducted via Differential Scanning Calorimetry (DSC) to measure the melting temperature and the occurrence of a single phase change. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) were employed to examine eutectic microstructures on a microscopic scale. Analysis of these results reveal that prediction of the composition and latent heat is possible.

2. Experimental methods

To prepare eutectics, anhydrous powders of the constituent salts¹

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¹ Sources and purity of these are listed in Table 1.

Table 1
Single salt source and purity.

Salt	Purity (wt%)	Source
NaCl	>99.9	Univar
KCl	>99.0	Chem-Supply Ltd
Na ₂ SO ₄	>99.0	Chem-Supply Ltd
Na ₂ CO ₃	>99.0	Chem-Supply Ltd
Li ₂ CO ₃	>99.0	Alfa Aesar
K ₂ CO ₃	>99.0	United Laboratories Inc.
NaNO ₃	>99.0	United Laboratories Inc.
LiNO ₃	>99.0	Chem-Supply Ltd
KNO ₃	>99.0	Chem-Supply Ltd

are dehydrated at 180 °C. The powders are then mixed according to the mass percent recommended by Factsage [7] for binary eutectics, and from various sources for ternary eutectics [8,9,3]. The powder mixture is placed into a 99.7% alumina crucible and placed in a furnace at a temperature 50 °C above the melting temperature reported in the literature for the eutectic composition. This temperature is chosen as it is below the decomposition temperature of the constituent salts, but provides a temperature differential large enough to provide the energy to melt the mixture.

The mixture is periodically checked until it is fully molten, typically 24 h. Then the crucible is removed from the furnace and the molten salt is poured onto a clean metal surface to cool and solidify. At least three independent DSC samples were tested in sizes ranging from 8 to 18 mg. These samples are removed from the greater melt and placed into 99.7% DSC alumina crucibles for DSC testing. These DSC crucibles are then sealed using a thin cap of wet potters clay. Clay lids are used to prevent sample creep, and were confirmed to not have any features visible by the DSC once baked above 450 °C. For samples less than 4 mg, or with a melting point below 500 °C, no clay lid was used, as samples did not creep out of the crucible.

The clay lid is allowed to dry for thirty minutes, and then the samples are placed into a Seteram Labsys 13 DSC, with nitrogen used as a purge gas. The samples are heated to 60 degrees below their melting point, and held isothermal for 45 min to sinter the clay. The samples are then ramped at 10 °C/min to a temperature approximately 10 degrees after the completion of the melting process, then immediately brought back down to 30 °C at the fastest cooling rate available (20 °C/min). This experimental procedure reduces the amount of time the sample is molten, reducing creep, whilst still providing the linear regions before and after the melting feature.

To calculate latent heat, the onset and completion temperatures must be calculated. This is done by fitting linear equations to the regions before and after the melting feature. The points where the data deviates from the fitted line are chosen as the melting onset and completion temperatures. A line joining these points acts as a baseline for the integration of the DSC curve. This integrated value is divided by the sample size and multiplied by the correlation factor to determine the latent heat. The temperature at which the melting features of the DSC curve disappear is calculated for the purposes of determining the latent heat. However, this depends strongly on sample size [10] and is thusly not reported. Larger samples take longer to melt, as the temperature distribution inside the sample is not as homogeneous as smaller samples. Thus, more time is required to provide the energy for the phase transition. The correlation factor is determined via the melting of 99.999% pure aluminum samples, both before and after testing of salt samples. Drift in this correlation factor is included in the calculation of experimental uncertainty.

Uncertainty in the DSC measurements is a combination of the standard deviation of the individual experiments, the drift in the correlation factor, and the uncertainty of the mass measurements. This is calculated via standard equations and is uniformly ± 8% across all samples.

SEM and EDS analysis is undertaken with a Zeiss Sigma Variable Pressure Field Emission SEM and an Oxford XMax 50 Silicon Drift EDS detector. From the melt, samples are selected which are large enough to polish opposing faces flat and parallel. Polishing is conducted with 500 grit SiO₂ sandpaper. As solid salts are electrical insulators, the electrons fired at the sample take time to disperse. Occasionally, the sample may become locally overcharged, leading to an overloaded detector. To reduce this overcharging, samples are partially covered with carbon tape and electron backscatter and EDS imagery is conducted close to the tape.

3. Theory

Previously described methods for predicting latent heat and for predicting the composition of a ternary eutectic are presented in the following section. The method for prediction of composition is chosen as it requires less experimental data and has been shown to be accurate for several multi-component mixtures [11]. Reciprocal mixtures consist of all possible combinations of anions and cations in the definition. For example, KCl and NaF can combine to form a quaternary eutectic KF + NaF + KCl + NaCl. The latter mixture is reciprocal, while the former is not. Reciprocal fluoride mixtures have been shown to have large heats of mixing, thus this work ignores them as possible candidates. Combining fluoride salt species leads to dramatically reduced latent heats in comparison to the individual components, lessening the effectiveness of combinations. In addition, previous work has predicted the latent heat [12,13] for reciprocal fluoride mixtures.

3.1. Latent heat

As storing energy is the primary objective of interest in LHTESS, the amount of energy that can be stored is the primary property of any potential PCM. Thus, predicting this property is extremely valuable. Kosa et al. [14] developed an equation to estimate the enthalpy of fusion for binary eutectics. Their results were based on the assumption that the entropy of the mixture was the same as the entropy of the individual components, plus an additional term for the entropy due to mixing of differentiable species. This assumption generalizes to the assumption that the heat of mixing is zero. Several authors disagree, finding this assumption to be over-generalized [15]. However, we will proceed with this assumption as it will be shown later to be almost exclusively accurate when fluoride mixtures are disregarded. Presented here is an equation expanded to n-component eutectics, in order to compare more possible mixtures:

$$\Delta H_{fus} = T_{fus} \cdot \sum_i^n x_i \cdot (\Delta S_{f,i} - R \cdot \ln(a_i \cdot x_i)) \quad (1)$$

where T_{fus} is the melting temperature of the eutectic, T_i is the melting temperature, $\Delta S_{f,i} = \frac{\Delta H_{f,i}}{T_i}$ is the entropy of fusion, x_i is the molar concentration, R is the universal gas constant, and a_i is the activity coefficient, all for the i^{th} component. Originally Kosa et al. found the best agreement by assuming the activity is unity. Further analysis with more mixtures finds this assumption can lead to poor agreement. The activity coefficient is determined via an application of Raoult's law, given a known composition:

$$a_i = \frac{1}{x_i} \cdot \exp\left(\frac{\Delta H_{f,i}}{R \cdot T_i} - \frac{\Delta H_{f,i}}{R \cdot T_{fus}}\right) \quad (2)$$

Substitution of Eq. (2) into Eq. (1) leads directly to a latent heat determined via:

$$\Delta H_{fus} = \sum_i^n x_i \cdot \Delta H_i \quad (3)$$

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