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Thermodynamic modeling of nitrate materials for hybrid thermal energy storage: Using latent and sensible mechanisms

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ABSTRACT

Applications for thermal energy storage (TES) are often found in nitrate salts which show high specific heat and high thermal stability over a wide temperature range, such as in the case of solar salt ($NaNO_3$-KNO_3). However, the combination of both sensible and latent heat capacity is desired since it increases the energy storage performance over the value of each of the mechanisms apart. We use CALPHAD thermodynamic modeling to study the role of this hybrid storage capacity in ternary nitrates composed by the solar salt and either $CsNO_3$ or $LiNO_3$ along certain compositional lines. For most cases, the highest amount of stored energy is for the pure sensible mechanisms; however, at $NaNO_3$ and $LiNO_3$ rich conditions for the $NaNO_3$-KNO_3-$CsNO_3$ and $NaNO_3$-KNO_3-$LiNO_3$ systems, respectively, we obtain that latent mechanisms increases up to 3% the value of the pure sensible mechanism. This estimation can shed light into novel procedures to find more effective materials for energy storage, and we expect new experimental measurements will be conducted to validate these criteria.

1. Introduction

1.1. Background and application

Alkali nitrates are important compounds for thermal energy storage (TES), in particular for sensible and latent storage applications since they show high values of melting temperature and thermal stability which define the lower and upper limit of the operating temperatures (Pfleger et al., 2015). In the case of sensible storage media, the heat storage is proportional to the heat capacity (C_P), which increases as the temperature increases (latent heat mechanisms excluded). Similarly important is the thermal decomposition (or stability), which depends on many parameters such as the polarization power that can be altered by a suitable choice of the cation. This possibility brings the nitrate salts a capability to examine the (thermal) properties by means of composition design with the aid of thermodynamic tools, such as the Computer Coupling of Phase Diagrams and Thermochemistry (CALPHAD) method. Additionally, the salt stability varies with the polarization power, which depends directly on the radius and is inversely proportional to the charge of the cation (Pfleger et al., 2015). Therefore, one important research aim is to select the nitrate ion so as to increase the system stability, namely the highest decomposition temperature, by choosing an appropriate alkali radius and charge. Another objective within the ion phase space research is to reduce the liquidus temperature (Tliq) in order to avoid salts freezing (Bauer et al., 2012), which is one of the main concerns in molten salts solar power plants (Moore et al., 2010). A common method to reduce the Tliq of the salt is by increasing the number of ions; however, this also increases the computational cost and difficulties to fully determine the phase diagrams.

In recent years, a new type of solar power plants that work with the so-called solar salt, a eutectic molten salt mixture consisting of 60 wt% sodium nitrate ($NaNO_3$) and 40 wt% potassium nitrate (KNO_3), are becoming widely extended (Herrmann et al., 2004; Lata et al., 2008; Cáceres et al., 2013). The eutectic mixture has a liquidus temperature of about 240 °C, and the temperature limit of thermal decomposition is about 550 °C, which allows for a working temperature between 250 and 500 °C, approximately (Pfleger

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et al., 2015). However, the Tliq is still high and, thus, implies extra costs in TES applications.

On the other hand, other approaches relying on the identification of suitable systems that can store energy not only in the form of sensible heat, but also as latent heat, are currently under consideration. In latent storage systems, the melting temperature defines the temperature at which the heat is stored. In these materials, the total amount of energy stored during the phase change can be more than one order of magnitude larger than that for the sensible heat form in a 10 K range, making the combination of both really appealing. Although the combination of sensible and latent heat has been already suggested as an alternative for improving the performance of alkali nitrates, most of the thermodynamic studies in these species have focused on sensible heat storage applications, while here we will estimate the total heat storage, this is, including the latent heat mechanisms. Thus, the methodology used in this work, can be used to enhance the design of TES devices, optimizing the total energy density by storing heat in the form of sensible and latent heat.

This work is structured as follows. The modeling techniques of multinary compounds is described in Section 2, including the phase diagrams and thermodynamic properties of constituting nitrate phases. In Section 3, based on pure to binary, to ternary, and then to multinary alikali nitrates (depending on the type of the solar salt) studies, we review the most relevant cases in the literature regarding the compositional studies, which is then used to assess our database. In Section 4 we use this database to provide estimates for the heat storage, including both the latent and specific heat, by calculating the contributions of the fusion enthalpy and specific heat in a temperature range along specific compositional lines.

1.2. Crystal structure

The crystal structure information and thermodynamic properties of pure nitrates have been critically reviewed and studied in a previous research by Helali et al. (2011) and Jriri et al. (1999). The pure nitrate $NaNO_3$ exhibits two stable crystalline rhombohedral forms at normal pressure (i.e., $\alpha NaNO_3$ at low temperature and $\beta NaNO_3$ at high temperature), with the same structure for αKNO_3 and βKNO_3. The $CsNO_3$ also shows two different crystalline structures, namely a hexagonal form at low temperature and a cubic form at high temperature, respectively. $LiNO_3$ only has one single stable crystalline rhombohedral structure. The most reliable crystal information are listed in Table 1.

In binary systems, the experimental phase diagrams and thermodynamic properties data have been critically reviewed and completely evaluated by several authors (Helali et al., 2011; Coscia and Elliott, 2015). For the $NaNO_3$-KNO_3 binary system, the eutectic temperature and composition has been extensively analyzed in the literature Guthrie (1884) and Hissink (1900), and summarized by Jriri et al. (1999). Moreover, besides the liquidus temperature, the enthalpy of formation of liquid and solid were also determined by thermal analysis in Briscoe and Madgin (1923), Zamali and Jemal (1994), Aghai-Khafri et al. (1974), and Kleppa and Hersh (1962), and used in our assessment procedure. Meanwhile, Jriri et al. (1999) also investigated experimental data about the $CsNO_3$-KNO_3 and $CsNO_3$-$NaNO_3$ binary systems, with the liquidus temperature measured following a differential thermal analysis (DTA) in the cases of $CsNO_3$-KNO_3 Zamali and Jemal (1994), Bol'shakov et al. (1961), Khvostova et al. (1974) and $CsNO_3$-$NaNO_3$ Bol'shakov et al. (1961), Nurminskii and Diogenov (1960), Diogenov and Sarapulova (1965), and Jriri et al. (1995b), as well as the transition temperatures Jriri et al. (1995b) and Belai-Drira et al. (1995). All the experimental values were used in the optimization process. Regarding the $LiNO_3$-$NaNO_3$ binary system, the experimental phase diagram, the composition, and the excess of free energy were also analyzed (Vallet, 1972; Bélaïd-Drira et al., 1996; Lesourd, 1976). As for the $LiNO_3$-KNO_3 binary system, there exists few experimental information for it was usually regarded as a simple eutectic reaction by Maeso and Largo (1993). Then, Zhang et al. (2002) carried out relative experiments to the eutectic and liquidus temperatures using the Differential Scanning Calorimeter (DSC). Afterwards, Coscia and Elliott (2015) reviewed the relative experimental information about the eutectic point (Vallet, 1972; Zhang et al., 2002; Xu and Chen, 1999), and predicted the phase diagrams for the $LiNO_3$-KNO_3 binary system with the use of mathematical models derived from the Gibbs free energy minimization. Moreover, the mixing enthalpies of the liquid phase of $LiNO_3$-$NaNO_3$ and $LiNO_3$-KNO_3 binary systems were measured by Meschel and Kleppa (1968) and Kleppa and Hersh (1962) at 623 K, respectively. All the experimental values were accounted for our optimization process.

Regarding ternary systems, as is the case of $CsNO_3$-$NaNO_3$-KNO_3, the liquidus points, a ternary eutectic reaction and the enthalpies of formation were determined using a visual polythermal method (Diogenov and Sarapulova, 1965), thermographic method (Mendeleva et al., 1973), and by reaction calorimetry method respectively of ternary liquid (Jriri et al., 1994). Regarding the $LiNO_3$-$NaNO_3$-KNO_3 ternary system, the eutectic point was measured by several authors (Carveth, 1898; Bradshaw and Meeker, 1990). Combing the previous literature, Mantha et al. (2012) designed and characterized thermally stable ternary nitrate heat transfer fluids (HTFs), which were then employed in order to mathematically derive the eutectic point. These results were also adopted in this work.

Besides ternary compounds, in a higher phase space, such as quaternary or quinary (including both nitrate and nitrite anions),

Table 1
Crystal information of pure nitrates.

Phase	$NaNO_3$			KNO_3		
	Structure	Lattice parameter, nm (Newns and Staveley, 1966)		Structure	Lattice parameters, nm (Newns and Staveley, 1966)	
		(a), nm	(α)		(a), nm	(α)
α phase-L	Rhombohedral	0.405	77°28′	Rhombohedral	0.446	74°
β phase-H	Rhombohedral	0.415	75°31′	Rhombohedral	0.449	73°50′
Phase	$CsNO_3$			$LiNO_3$		
	Structure	Lattice parameter, nm (Newns and Staveley, 1966)		Structure	Lattice parameters, nm (Jriri et al., 1995a)	
		(a), nm	(b), nm		(a), nm	(α)
α phase-L	Hexagonal	1.087	0.776	Rhombohedral		
(one stable form)	0.547	48°3′				
β phase-H	Cubic	0.449	–			