

# Thermal stability of potassium and sodium nitrate molten salt mixtures above 500°C

Steven Wright<sup>1\*</sup>, Ty Tran<sup>1</sup>, Chunlin Chen<sup>1</sup>, Rene Olivares<sup>2</sup>, and Shouyi Sun<sup>1</sup>

*CSIRO Energy Transformed Flagship*

1) *CSIRO Process Science and Engineering, Bayview Ave, Clayton, Vic 3169, Australia*

2) *CSIRO Energy Technology, 10 Murray Dwyer Circuit, Mayfield West, NSW 2304, Australia*

**Abstract:** Nitrate based salts have application as a heat transfer fluid for solar field applications and are normally used up to maximum temperatures of 500°C. There is improved thermodynamic efficiency if the upper operating temperature of these working fluids can be increased. This paper explores the high temperature stability of binary KNO<sub>3</sub>-NaNO<sub>3</sub> salt mixtures, the effect of atmosphere on the NO<sub>x</sub> evolution and the effect of additives to the melt. Several experimental techniques were used including combined thermo-gravimetric and evolved gas analysis; at the milligram and larger twenty gram scale, where the melt stability was examined at temperatures as high as 1000°C.

The general findings are that the binary KNO<sub>3</sub>-NaNO<sub>3</sub> molten salt mixture is stable up to temperatures of 500°C, with very little weight change of the melt, although there was some evolved NO<sub>x</sub> gases over this temperature range. The use of pure dry nitrogen or air as a protective atmosphere was more effective, reducing NO<sub>x</sub> evolution over the entire temperature range than pure argon gas. At temperatures above 500°C, there is significant evolution of NO<sub>x</sub> species in the gas and a large weight change observed for the melt. However the weight change far exceeds that expected for nitrate salt decomposition and there is clear evidence that nitrate salt evaporation may be the dominant factor in decreasing melt stability.

The thermo-gravimetric studies where the molten salt was progressively heated to 1000°C indicated that carbonate addition to the melt (as a mixture of K<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub>) may have increased the thermal stability of the melt. This was explored further in a series of experiments where the molten salt mixtures were heated to between 500 and 700°C and held at temperature for two hours to examine weight loss rates of the salt mixtures.

The experimental results are also compared with thermodynamic predictions from a general molten salt thermodynamic solution model based on the Cell model being developed by CSIRO. The main purpose of this modeling is to aid in finding and determining the potential operating window of a complex molten salt mixture where the melt is chemically stable.

**Key words:** molten salt, potassium nitrate, sodium nitrate, sodium carbonate, potassium carbonate, heat transfer,

## 1. Introduction

Commercial solar thermal plants which concentrate the sun's energy to produce steam and electricity use molten salt mixtures as a heat transfer fluid (HTF) or for thermal energy storage. These plants mainly use nitrate based melts that operate at temperatures below 500°C [1- 7]. Operating these salts at temperatures higher than 600°C may be possible by rigorous control of the atmosphere under which they are used [8]. However, a salt that is stable at higher temperatures

than 700°C is needed to make effective use of, for example, high temperature closed-loop Brayton power cycles or Rankine cycles using supercritical steam to potentially increase the heat-to-electricity conversion efficiency.

This paper documents preliminary investigations on a sodium nitrate/potassium nitrate HTF and storage fluid with the goal of trying to develop a formulation to extend the upper temperature range beyond 500°C. There have been numerous studies and patents reported in the literature on melt chemistries to reduce the eutectic temperature of potassium nitrate-sodium nitrate mixture [9,10] and on extending the upper working temperature by adding other salts and controlling the nitrate to nitrite ratio [11-15] in the melt. The studies have relied heavily on combined differential scanning calorimetry and thermogravimetric analysis[4,8,15-17] and used a relatively small quantity of melt (<500 mg) to evaluate the melt stability. This work describes the use of a larger scale thermogravimetric apparatus combined with evolved gas analysis for NO<sub>x</sub> where a more substantial twenty gram quantity of melt was used to evaluate melt stability.

In addition to the experimental studies, a solution model for the nitrate-carbonate-chloride-sulphate-hydroxide molten salt has been developed. The model parameters were optimized against the published phase diagrams [10]. With the model, the CSIRO developed software: Multi-Phase Equilibrium (MPE) was used to evaluate the stability of the nitrates system under various conditions [18] studied in this paper.

## 2. Thermodynamic modeling

The Multi-Phase Equilibrium (MPE) is software developed at CSIRO for calculating the chemical equilibrium in complex multi-phase multi-component systems [18]. For the purpose of using MPE in evaluating the effect of various additives on the nitrate decomposition and evaporation, a thermodynamic model and database for the nitrate salt solution needs to be developed. The cell model [19] which is capable of modelling the solutions with multi-cations and anions was used for describing the molten salt phase in this study. The cell model required interaction parameters between nitrates and possible additives such as chlorides, hydroxides, sulphates and carbonates to be optimized. With the database, the MPE was used to calculate the chemical equilibrium of the nitrates system under various conditions.

Beyond the decomposition of the nitrates, the evaporation of the nitrates at high temperature could be another limitation on extending the upper temperature range of application of nitrates salt. Figure 1a shows the variations of the NaNO<sub>3</sub> and KNO<sub>3</sub> vapour pressure with the temperature equilibrated with the pure NaNO<sub>3</sub> and KNO<sub>3</sub>. The NaNO<sub>3</sub> and KNO<sub>3</sub> vapor pressures increased by two orders of magnitude with the temperature increasing from 500 to 700 C.

Figure 1b shows that the lowest melting temperature of the base NaNO<sub>3</sub>-KNO<sub>3</sub> system is about 223°C at the equimolar composition. Therefore, the NaNO<sub>3</sub>-KNO<sub>3</sub> equimolar mixture was used as a base case in this study for comparing the stability of the molten salts under various conditions. The model parameters of NaNO<sub>3</sub>-KNO<sub>3</sub> interaction are optimized against the published NaNO<sub>3</sub>-KNO<sub>3</sub> phase diagram [20] and are a good representation of the phase diagram.

The KNO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> and NaNO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> interaction parameters of the model were optimized by fitting the published phase diagrams [10]. The Gibbs free energy of the nitrate and carbonate species were adopted from SGTE database [21].

The nitrate-carbonate phase diagram is a simple eutectic system, and there are no stable compounds formed between sodium and potassium nitrate and carbonate, as shown in Figure 2a and Figure 2b. The interactions between nitrates and carbonates are very weak. Therefore, the addition of carbonates is not expected to change the stability of nitrates significantly.

Figure 3 shows that 5 wt% carbonate addition to the equimolar binary nitrate mixture only reduces the nitrite/nitrate ratio in the salt slightly, due to the dilution effect of the carbonate in the melt. The experimental measured nitrite/nitrate ratio in the  $\text{KNO}_3$ - $\text{NaNO}_3$  equimolar salt with 5 wt% carbonate addition by Olivares [22] was also plotted for comparison. These results show that the model can give a reasonably accurate prediction of nitrite/nitrate ratio in the nitrate salt over the temperature range of 500 to 700 C.

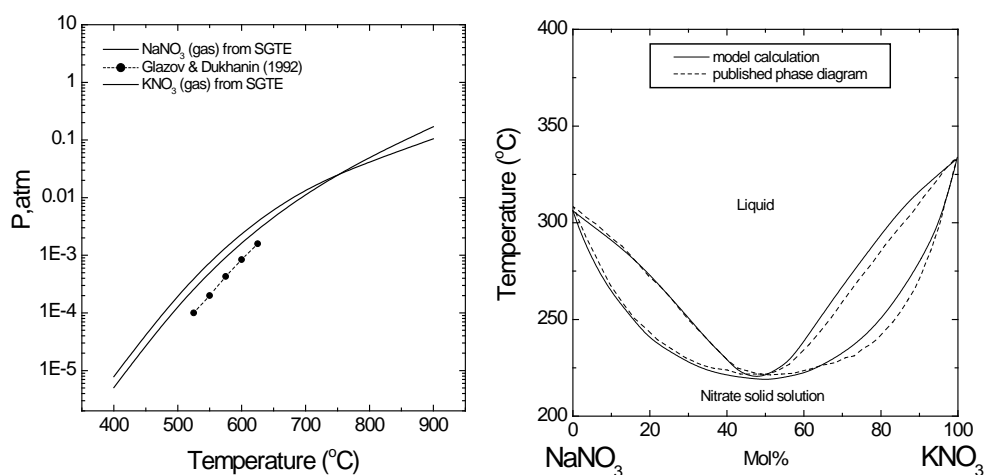


Figure 1. a) Partial pressures of the nitrates vapour over pure nitrates [21,22] b) The comparison of the calculated and published phase diagram of  $\text{NaNO}_3$ - $\text{KNO}_3$  system[20].

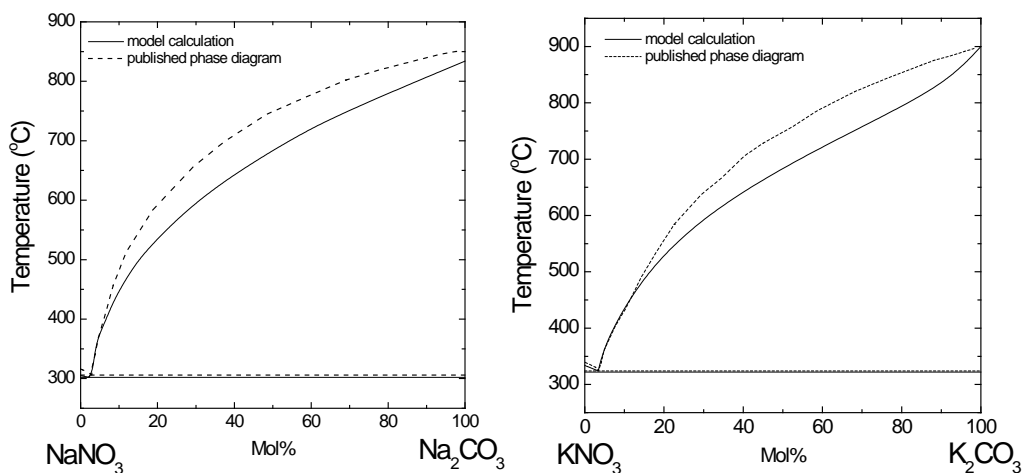


Figure 2. Comparison of calculated and published phase diagrams for the a)  $\text{NaNO}_3$ - $\text{Na}_2\text{CO}_3$  and b)  $\text{KNO}_3$ - $\text{K}_2\text{CO}_3$  systems [10]

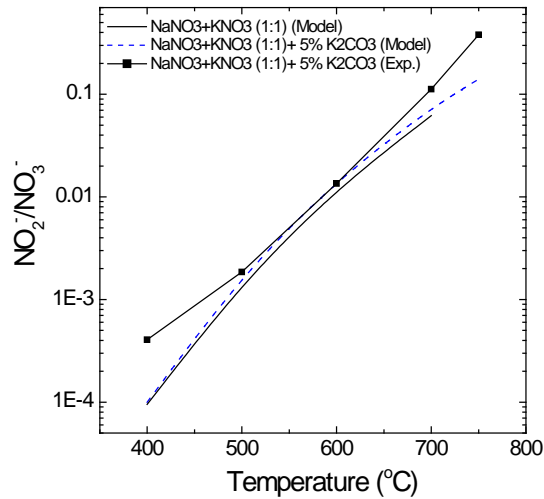


Figure 3. Effect of the carbonates on the nitrite/nitrate ratio of the salt.

### 3. Experimental

#### *Temperature scanning thermogravimetric study with NO<sub>x</sub> analysis*

A vertical tube furnace with a 100 mm diameter working tube with water cooled caps was used to perform the temperature scanning experiments. A twenty gram sample of the molten salt contained in an alumina crucible was suspended from a balance by molybdenum wire. A Pt/Pt-13%Rh thermocouple in a closed end alumina tube was located approx 10 mm alongside the suspended crucible to monitor the sample temperature. The entire suspended length of crucible, wire and the balance was enclosed to maintain atmosphere control. High purity argon gas was used to purge the working tube of air. The argon flow rate was controlled at 250 cm<sup>3</sup>/min into the furnace by a mass flow controller, and exited the furnace through bubblers to prevent air ingress into the furnace. A schematic of the experimental setup is shown in Figure 4.

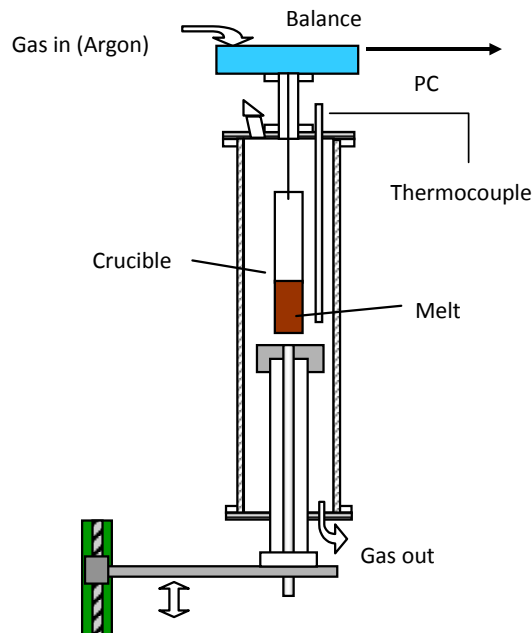


Figure 4. Experimental arrangement for the temperature scanning thermogravimetric study.

The furnace was heated at a rate of 10°C per minute until the salt sample was at a temperature of 1000°C. The weight change of the sample was measured by the balance and logged every 15 seconds to a computer. A Teledyne TH200 cathodo-luminescence NO<sub>x</sub> analyser was used to measure the NO, NO<sub>2</sub> and N<sub>2</sub>O contents in the gas from the furnace. The furnace and sample temperatures, and the NO, N<sub>2</sub>O and NO<sub>2</sub> concentrations were stored using a data logger. When the sample temperature reached 1000°C, the temperature, weight and gas analysis logging were halted and the furnace allowed to cool under natural convection to room temperature. The effect of gas atmosphere and pN<sub>2</sub> and pO<sub>2</sub> was investigated on the salt mixtures, by using Ar, N<sub>2</sub> or air flowing over the molten salt mixture.

A mixture of pure reagent grade KNO<sub>3</sub>-NaNO<sub>3</sub> in the weight proportions 54.33-45.67, from pre-dried reagents at 105°C was prepared by weighing into a clean dry jar and then mixed by rolling for 10 minutes. The salt mixture was then transferred to the alumina crucible to be used in the experiment. At the completion of the experiment, when the crucible had returned to ambient temperature, the crucible was removed from the furnace and re-weighed to confirm the mass loss measured by the suspension balance. Melts of KNO<sub>3</sub>-NaNO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> in the weight proportions of 51.61-43.49-2.83-2.17 were also prepared for study.

#### *Thermal equilibrium thermogravimetric study*

After the initial thermogravimetric study, a second series of experiments were undertaken to investigate the evaporation rate from the molten salt mixture in the 20 gram thermogravimetric apparatus. The molten salt was heated to a desired temperature and the mixture allowed to thermally equilibrate over several hours and measure the weight loss from the sample. The rate of weight loss was investigated at temperatures between 500 and 750°C under a flowing nitrogen atmosphere.

## **4. Results**

#### *Temperature scanning thermogravimetric study with NO<sub>x</sub> analysis*

The thermal stability of the 50 mol% reference case was investigated under Ar, N<sub>2</sub> and air atmospheres. The nitrogen species that had the highest concentration in all the tests was NO<sub>x</sub>, with the concentrations measured under an argon atmosphere shown in Figure 5a. The effect of gas atmosphere on the stability of the NO<sub>x</sub> species was significant, an air or nitrogen atmosphere suppressed the formation of NO<sub>x</sub> species in the gas phase. Figure 5b shows that the concentration of the major species (NO<sub>x</sub>) was decreased by at least a factor of 40 by using air or nitrogen. The weight change of the melts under the 3 different atmospheres and the rate of weight change is shown in Figure 6.

The average NO<sub>x</sub> concentration for the Ar experiment over the entire heating period was 360 ppm, then the number of moles of N decomposed was  $(360/1 \times 10^6) \times 0.25 \times 120/22.4 = 4.8 \times 10^{-4}$  moles or 0.03 g, equivalent to 0.15% of the sample weight. As the average NO concentration was 355 ppm and the average NO<sub>2</sub> was 2 ppm, the total weight loss due to decomposition of nitrate salt to produce NO<sub>x</sub> was ~ 0.3%. The mass of salt decomposing to evolve NO<sub>x</sub> was far less for the N<sub>2</sub> and air experiments.

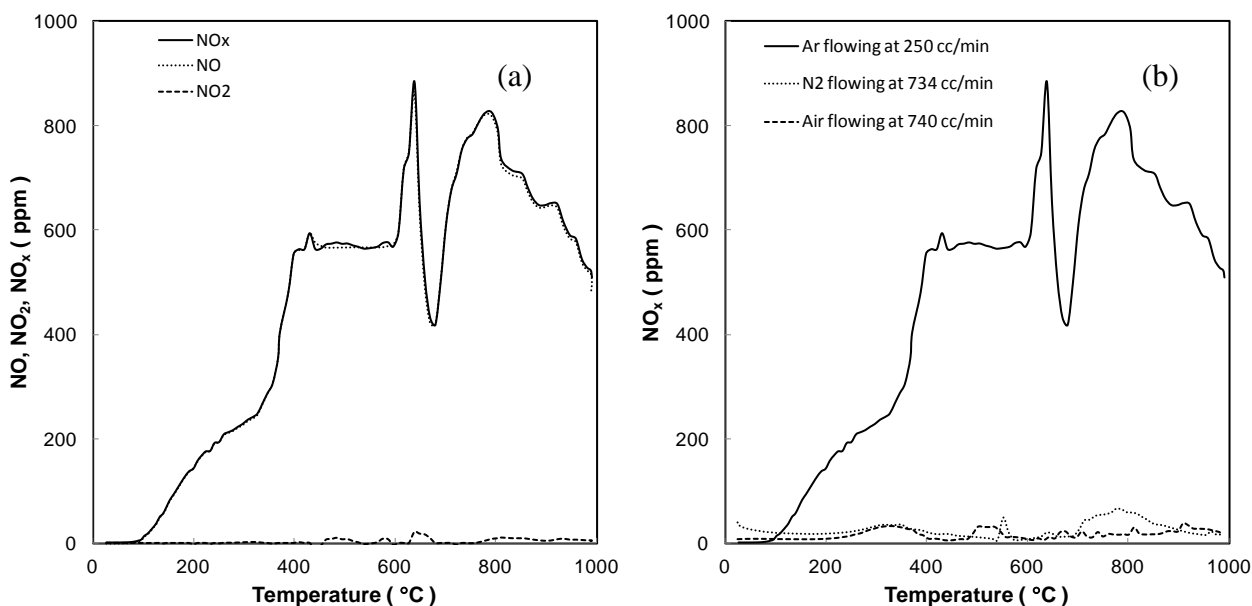


Figure 5. a) Measured NO, NO<sub>x</sub> and NO<sub>2</sub> concentrations during the thermal stability studies of a 50 mol% NaNO<sub>3</sub>-KNO<sub>3</sub> salt mixture under Ar flowing at 250 cm<sup>3</sup> min<sup>-1</sup>. b) Measured NO<sub>x</sub> concentrations during the thermal stability studies of a 50 mol% NaNO<sub>3</sub>-KNO<sub>3</sub> salt mixture under Ar, N<sub>2</sub> and air.

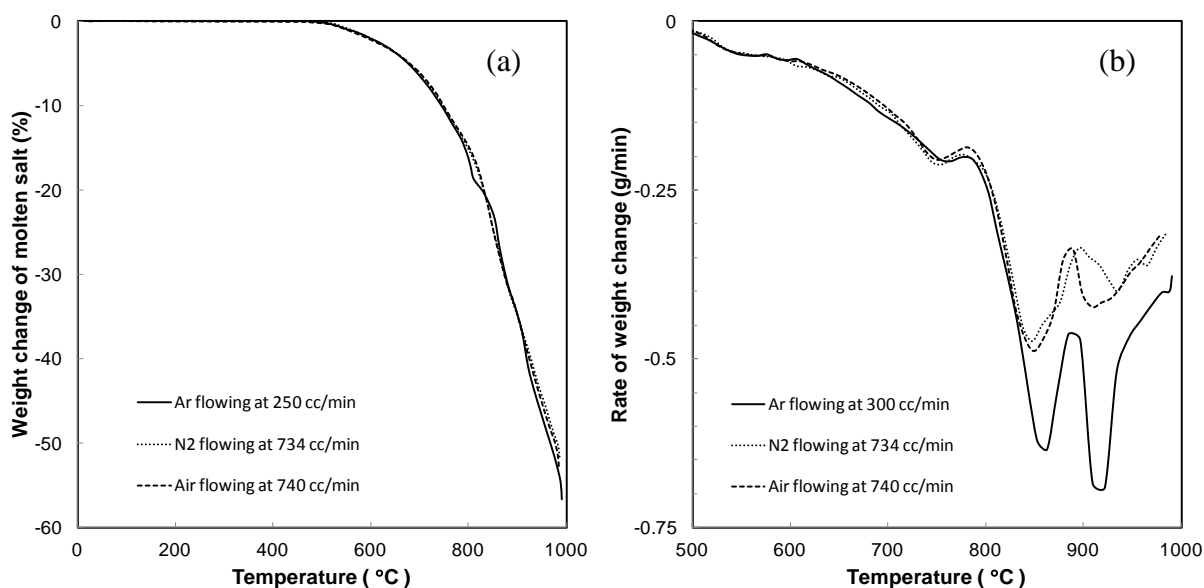
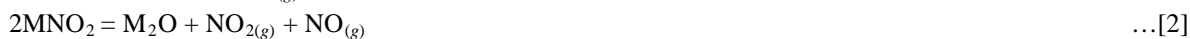


Figure 6. a) Plot of weight change with temperature for 50 mol% NaNO<sub>3</sub>-KNO<sub>3</sub> under Ar, N<sub>2</sub> or air atmospheres. b) Plot of rate of weight change with temperature for 50 mol% NaNO<sub>3</sub>-KNO<sub>3</sub> under Ar, N<sub>2</sub> or air atmospheres.

It is possible for the nitrate to decompose to evolve oxygen and nitrogen via the following reactions:



Evolved gas analysis on the binary nitrate salt mixture has been performed by Olivares using a quadrupole mass spectrometer [8]. Under Ar atmospheres, O<sub>2</sub> and N<sub>2</sub> as well as NO and N<sub>2</sub>O were observed as gaseous products from the

salt decomposition. The magnitude of the evolution of  $O_2$  and  $N_2$  was less than an order of magnitude of that for  $NO$ . Under nitrogen atmospheres, oxygen evolution followed the same trend as reported above, but was significantly reduced, and it was not possible to determine if the ratio of  $O_2$  to  $N_2$  altered when air was used as the atmosphere. When air or nitrogen atmospheres are used, the decomposition of the salt becomes thermodynamically less favourable, and although not directly measured in this study, it is a reasonable assumption that the weight loss due to reactions 1 to 4, is of the same order as that due to the nitrate decomposing to  $NO$ ,  $NO_x$  and  $N_2O$  which were measured in this study.

The temperatures at which the weight loss of molten salt became significant (1%) were within 7 degrees for the 3 gas compositions studied, with an average temperature of  $553^\circ C$ . The rate of sample weight change with temperature is shown in Figure 6b, where the rate at which the melt loses weight becomes very high at temperatures above  $700^\circ C$ . At temperatures of  $850^\circ C$  and higher, the rate of sample loss decreased.

The results for the individual experiments on the binary nitrate doped with an equi-molar mix of  $Na_2CO_3$ - $K_2CO_3$  under Ar,  $N_2$  and air atmospheres are presented in Figure 7 and Figure 8. When compared with the binary nitrate mixture under an argon atmosphere, carbonate addition has reduced the  $NO_x$  concentration in the gas by a factor of at least 3. There is a slight increase in  $NO_x$  concentration in the gas for the carbonate containing melts under nitrogen or air compared to the binary reference salt shown in Figure 5b. The effect of gas atmosphere on the weight change of the carbonate containing nitrate melt was negligible.

The temperature at which the carbonate containing melts had lost 1% mass occurred at 596, 612 and  $600^\circ C$  for Ar,  $N_2$  and Air atmospheres respectively. Compared with the binary nitrate melt, the carbonate containing nitrate salt would appear to be 50 degrees more stable under *non-equilibrium heating conditions*. Figure 8b shows that the rate of weight loss for the carbonate and the binary reference were similar, but there is an approximate 50 degree displacement of temperature. Unlike the binary nitrate melt, the trends of rate of change of the weight loss for the carbonate containing melts was nearly identical for all three gases studied.

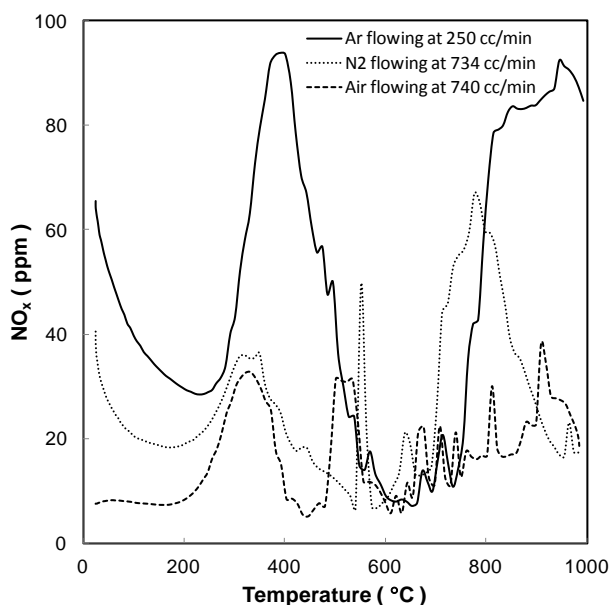


Figure 7. Measured  $NO_x$  concentrations during the thermal stability studies of a 48.1 mol%  $NaNO_3$ -48.1 mol%  $KNO_3$ -1.9 mol%  $Na_2CO_3$ - 1.9mol %  $K_2CO_3$  salt mixture under Ar,  $N_2$  and air.

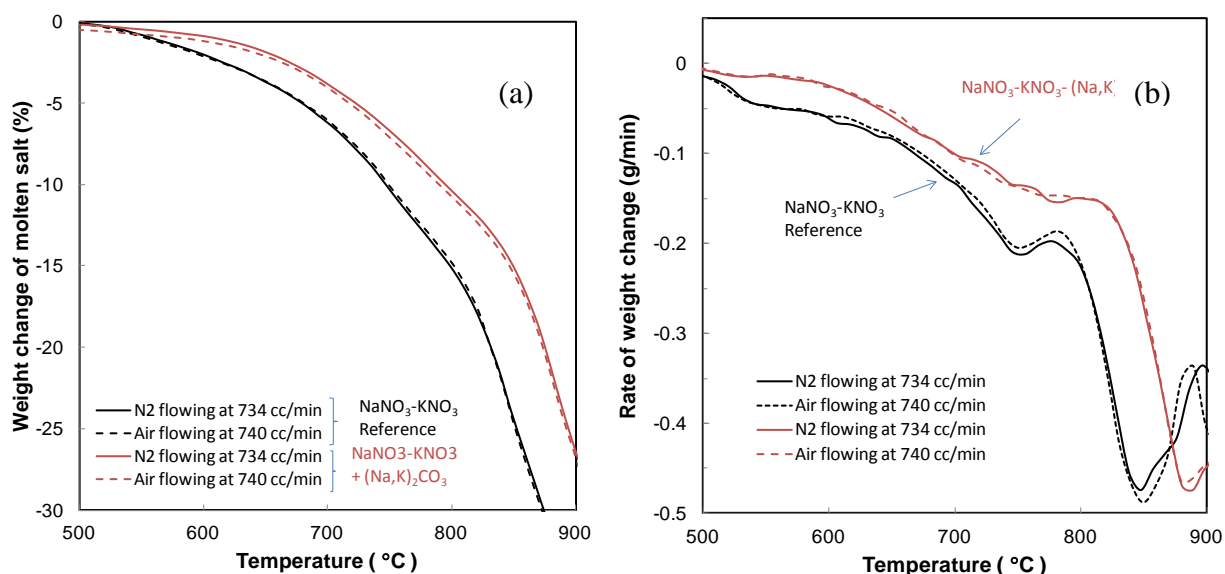


Figure 8 a) Plot of weight change with temperature for 48.1 mol%  $\text{NaNO}_3$ -48.1 mol%  $\text{KNO}_3$ -1.9 mol%  $\text{Na}_2\text{CO}_3$ - 1.9 mol%  $\text{K}_2\text{CO}_3$  under Ar,  $\text{N}_2$  or air atmospheres, compared with the weight change observed for 50 mol%  $\text{NaNO}_3$ -50 mol%  $\text{KNO}_3$ . b)Rate of weight change with temperature for a 48.1 mol%  $\text{NaNO}_3$ -48.1 mol%  $\text{KNO}_3$ -1.9 mol%  $\text{Na}_2\text{CO}_3$ - 1.9mol %  $\text{K}_2\text{CO}_3$  under Ar,  $\text{N}_2$  or air atmospheres and compared with the rate of weight change for the binary melt.

#### Thermal equilibrium thermogravimetric study

The weight loss observed for a 20 gram sample of 50 mol%  $\text{NaNO}_3$ -50 mol%  $\text{KNO}_3$  melt heated to temperatures between 520 and 720°C under a nitrogen atmosphere and maintained at that temperature for 2 hours is shown in Figure 9a, and the weight losses at the same temperatures for the binary nitrate melt containing carbonate are shown in Figure 9b. The weight loss rates at each temperature calculated over a period of constant temperature ( $\pm 2$  degrees ), shown solid lines in Figure 9. The weight loss rates are given in Table 1.

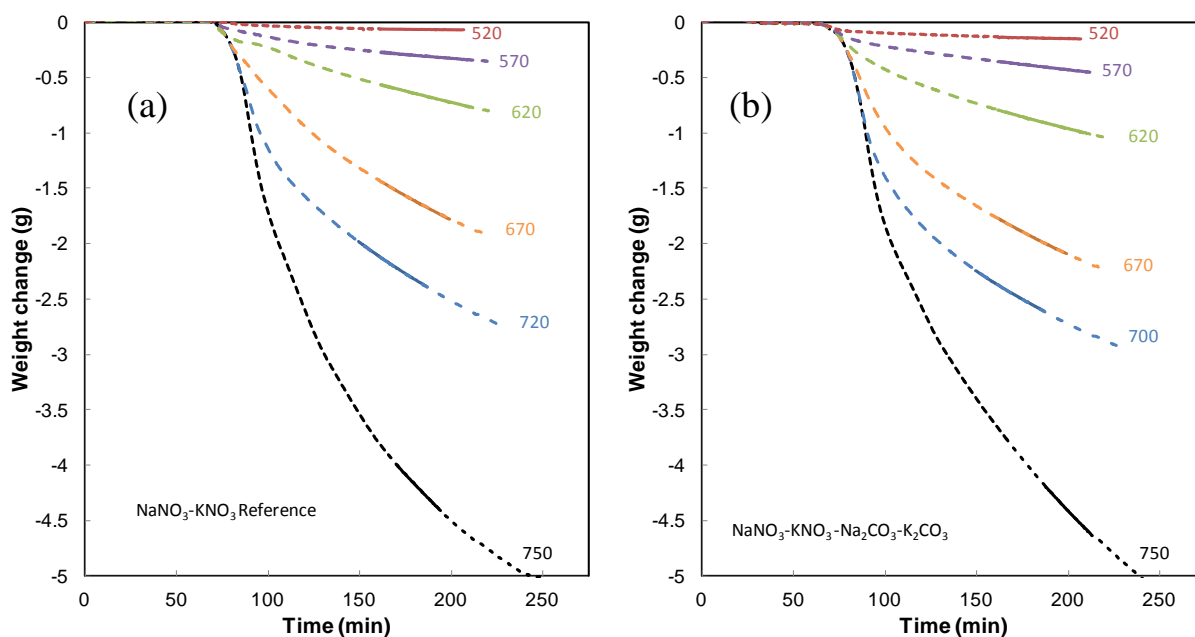


Figure 9. a) Plot of weight change with time for the binary  $\text{NaNO}_3\text{-KNO}_3$  reference melt under a nitrogen atmosphere heated to temperature and maintained at temperature for 2 hours (Solid line is constant temperature period). b) Plot of weight change for the binary melt containing carbonate components.



Table 1. Weight loss and rate of weight loss at constant temperature under a nitrogen atmosphere for the binary nitrate molten salt and the binary mixture containing carbonate.

	50 mol% NaNO <sub>3</sub> -50 mol% KNO <sub>3</sub>	48.1 mol% NaNO <sub>3</sub> -48.1 mol% KNO <sub>3</sub> -1.9 mol% Na <sub>2</sub> CO <sub>3</sub> -1.9 mol% K <sub>2</sub> CO <sub>3</sub>
Temperature (°C)	Rate of weight change (mg/min)	Rate of weight change (mg/min)
520	1±2	1±2
570	2.0±2	2.2±2
620	4.5±2	4.0±2
670	9.5±2	9.0±2
700		10.0±2
720	11.0±2	
750	17.0±4	18.0±4

Previous gas analysis results showed that weight loss from the melt due to nitrate decomposition was small, then most of the loss of weight is due to evaporation of volatile KNO<sub>3</sub> and NaNO<sub>3</sub> from the melt. An Arrhenius plot of the evaporation rate from the thermal equilibration experiments for the melts is compared with the rates measured from temperature scanning experiments in Figure 10. Within the uncertainty of the measurements, there is no difference in the evaporation rate of salt from the binary melt and the carbonate containing melt. The evaporation rates from the equilibrium experiments are an order of magnitude lower than that observed in Figure 8.

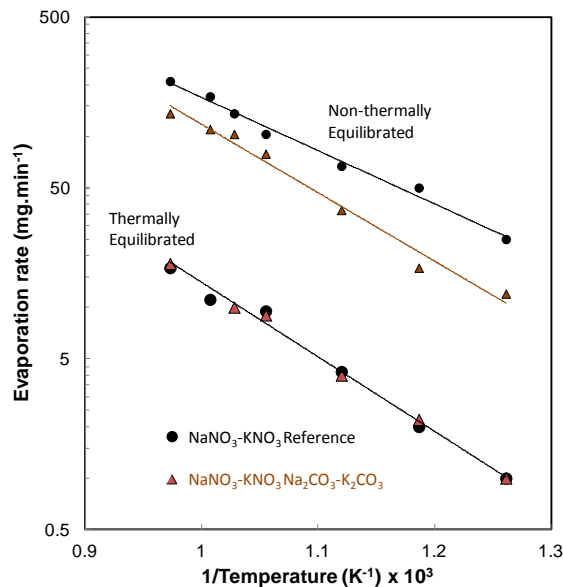
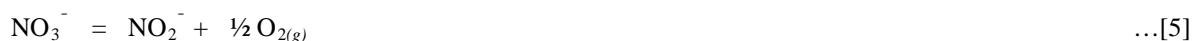


Figure 10. Arrhenius plot of the evaporation rate of salt from the thermal equilibration experiments and the thermal scan experiments for the binary nitrate melt and the nitrate melt containing carbonate.

## 5. Discussion

### *Nitrate-nitrite distribution and stability of binary KNO<sub>3</sub>-NaNO<sub>3</sub> melts*

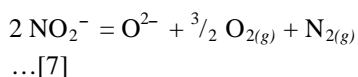
In nitrate based salts, the main decomposition reaction is the partial dissociation of nitrate-ion (NO<sub>3</sub><sup>-</sup>) to nitrite-ion (NO<sub>2</sub><sup>-</sup>) and oxygen (O<sub>2</sub>) according to Equation 5:



The shift from nitrate to nitrite occurs slowly and is limited by the partial pressure of oxygen in the atmosphere contacting the molten salt. The equilibrium constant for equation 5 is expressed as Equation 6;

$$K_{eq} = [\text{NO}_2^-] \cdot p\text{O}_2^{1/2} / [\text{NO}_3^-] \quad \dots[6]$$

The equilibrium ratio from Equation 6, for the equimolar mixture  $\text{NaNO}_3\text{-KNO}_3$  has been measured by Nissen and Meeker[23] over the temperature range 500-600°C. The upper temperature limit of complex nitrate mixtures is mainly a function of the equilibrium nitrate/nitrite ratio ( $\text{NO}_3^-/\text{NO}_2^-$ ). For example, in contact with air ( $p\text{O}_2$  of 0.21 atm) the equilibrium nitrite content in pseudo-binary  $\text{KNO}_3\text{-NaNO}_3$  is 1.1 mol% at 500°C. This concentration increases to 5.7 mol%  $\text{NO}_2$  at 600°C. Increasing the nitrite content, reduces the activity of  $\text{NO}_3^-$  in the melt and hence limits the extent of decomposition by reaction 1, which increases the upper temperature of the stability range. However in air, the nitrite ion is less stable than nitrate ion and can be decomposed or oxidised back to nitrate via the reverse reaction of Equation 1 or 5. A generalised decomposition reaction for nitrite can also be given by Equation 7:



In the work of Raade and Padowitz[13], the thermal stability of the sample was defined as the temperature at which the sample had lost a maximum of 3% of its weight during thermo-gravimetric analysis. Two atmospheres were used to study melt stability; air and nitrogen, with significant differences observed between them. Under the non-equilibrium heating conditions that occur in the small scale TGA measurement, mixtures containing nitrate/nitrite generally showed higher thermal stability when tested in air. This was attributed to the oxidation of nitrite to nitrate producing an increase in weight that masked the weight loss due to thermal decomposition.

This study shows that the composition of the gas atmosphere had a significant effect on the amount of  $\text{NO}_x$  formed during heating of a nitrate melt to temperatures of 1000°C. Mass spectroscopic analysis of gas in the binary system on a 3 gram melt sample of the reference binary mixture heated in an argon atmosphere observed that NO began forming at temperatures above 600°C,  $\text{N}_2$  and  $\text{O}_2$  at 630°C and  $\text{NO}_2$  at 670°C. The NO concentration was significantly greater than that measured for  $\text{NO}_2$  [8] and consistent with the  $\text{NO}_x$  gas analysis of this study. However in this study,  $\text{NO}_x$  was detected at lower temperatures than observed by Olivares[8]. Gordon and Campbell [24] have also reported evolution of nitreous fumes from the melt soon after melting, at temperatures of 100 to 300°C above the melting point. These results suggest that non-equilibrium thermal heating influences the nitrate (and nitrite) decomposition and the volatilisation of the salt.

The melt compositions studied in this work were not at chemical equilibrium during the temperature scanning experiments and it can be assumed the equilibration time may still not have been long enough during the thermal equilibration experiments for the  $\text{NO}_3^-/\text{NO}_2^-$  attain the equilibrium ratio. The nitrite ion concentration would be expected to be lower than the equilibrium content. This would tend to increase the activity of the nitrate ion and hence encourage melt decomposition by reactions 1 and 3. However, the large weight changes observed in this study compared to the low  $\text{NO}_x$  contents in the gas stream strongly suggest that salt evaporation is the dominant cause for mass loss at temperatures up to 1000°C. Although the decomposition reactions are of major concern for long term melt stability, they are of secondary importance in this study.

Although not measured directly by gas analysis, and inferred by the weight loss of the sample, this study shows that the major species in the gas during heating are the mixture components;  $\text{NaNO}_3$  or  $\text{KNO}_3$ . At 700°C, under thermal equilibrium conditions, the melt lost mass at a rate of  $10 \text{ mg}\cdot\text{min}^{-1}$  equivalent to losing 0.04% per minute to the vapour

phase. Assuming that the melt and vapour phases are in equilibrium ( $p_{\text{NaNO}_3}=p_{\text{KNO}_3}$ ), the partial pressure of  $\text{KNO}_3$  and  $\text{NaNO}_3$  was 0.0012 atm.

### *Stability of the binary nitrate containing carbonate*

Carbonate ( $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$ ) addition to nitrate melts does lower the liquidus temperature of the pure nitrate ( $\text{KNO}_3$  or  $\text{NaNO}_3$ ) with only slight solubility in the nitrate at temperatures close to the eutectic [10]. The solubility does increase substantially with temperature up to 800°C.

The experimental results of this study and of Olivares [8] suggest that during heating up to 1000°C, the carbonate containing melts are more stable with respect to  $\text{NO}_x$  evolution,  $\text{N}_2$  and  $\text{O}_2$  formation and weight loss. The onset of a 1% weight loss occurred at ~ 605°C, compared to 555°C for the reference melt. The  $\text{NO}_x$  measurements from the carbonate containing melts in this study were at much lower concentrations than the reference;  $\text{NO}$  evolution began at the onset of heating, but did not increase to the levels of the binary reference.

These results suggest that during heating conditions, the carbonate melts are more stable than the reference melt. However when the melts are at thermal equilibrium, Figure 10 shows that there was no difference on the evaporation rate from the binary or the carbonate containing nitrate melts. This also suggests that although carbonate addition should reduce the concentration of the nitrogen species ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ) in the melt, the activity of the species has not been reduced if  $p_{\text{KNO}_3}$  is equal to  $a_{\text{KNO}_3}$  and similarly for sodium nitrate.

Figure 11 compares the predicted weight change for the binary melt and the carbonate containing melts from the MPE thermodynamic model with the experimental data from this study. The experimental conditions (20g of salt heated at 10 C/min under  $\text{N}_2$  flow at 730 ml/min) are used in the model calculation. The predicted weight loss from vaporization and decomposition for the binary nitrate melt and the nitrate melt containing carbonate are nearly identical, which agree with the experimental measurements under thermal equilibrium listed in Table 1. The differences between the binary salt and the salt with carbonate addition are apparent only at temperatures above 800°C, which is due to the dilution effect of carbonate. The weight losses predicted by the equilibrium model are much less than the non-equilibrium experiments.

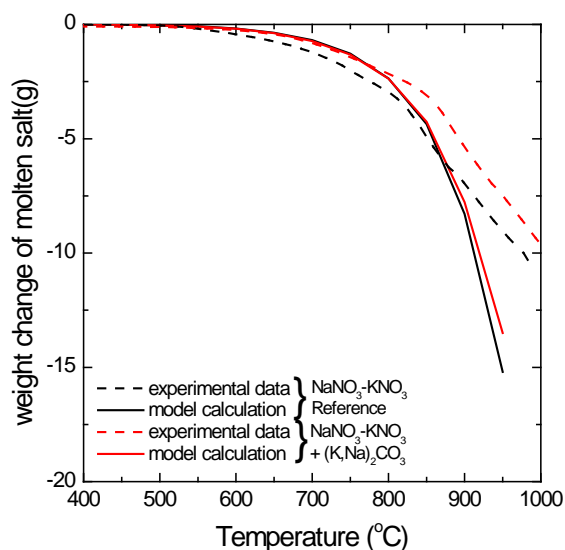


Figure 11. Effect of the Carbonates on the stability of the binary  $\text{NaNO}_3$ - $\text{KNO}_3$  salt.

The possible cause for the apparent stability of the carbonate containing melts during non equilibrium heating may be due to the low solubility of carbonate in the melt which increases with increasing temperature. Carbonate crystals dissolve in the melt during heating and this requires additional energy compared to heating the binary  $\text{NaNO}_3$ - $\text{KNO}_3$  melt, so the actual temperature of the carbonate containing melt may be lower than the reference melt.

#### *Process implications of nitrate decomposition and high salt volatility*

The use of nitrogen or air as a blanketing gas fixes the  $p_{\text{N}_2}$ ,  $p_{\text{O}_2}$  (or both) and reduced the decomposition of nitrate in the melt to produce  $\text{NO}_x$ . With a nitrogen atmosphere, the average  $\text{NO}_x$  partial pressure over the 250-750°C temperature range was 25 ppm, equating to a decomposition rate of 1% per day. With an air atmosphere, the average concentration was 17 ppm. Carbonate addition did not reduce the average  $\text{NO}_x$  concentration, which was 40 ppm over the 250-750°C temperature range, equivalent to 1.6% of the salt decomposing per day. Even a 1% decomposition rate may possibly be too high for practical purposes in solar heat transfer/storage applications.

Although the decomposition of the nitrate salt to  $\text{NO}_x$  at temperatures above 700°C is not a major contribution to weight loss, the molten salt will still not be stable enough for long term use as a heat transfer fluid. Furthermore, the volatility of the salt at these temperatures will also be a significant operational difficulty. From the data at 700°C, the molten binary nitrate salt lost mass at a rate of 0.04-0.06 % per minute, with a partial pressure in the gas of 0.0012 atm of  $\text{NaNO}_3$  and  $\text{KNO}_3$ . This equates to over 55 to 85% of the mass of salt per day.

These calculations are based on a relatively large proportion of gas to melt (approximately 20 times ratios<sup>0</sup> used in the current experimental study. In solar applications the proportion of gas to melt may be much smaller than 0.1, as liquid salt is pumped around the thermal storage loop. The mass of salt decomposing or volatilising in such situations may be far less.

## **6. Conclusions**

The impacts on the thermal stability of a binary  $\text{NaNO}_3$ - $\text{KNO}_3$  reference melt at the eutectic composition of various formulations were:

- The use of air or nitrogen decreased the concentration of  $\text{NO}_x$  in the gas phase from the thermal decomposition of the nitrate salts in the melt.
- For all the melt compositions studied, during heating to 1000°C, the weight loss from the melt, far exceeded the mass lost due to nitrate salt decomposition to  $\text{NO}_x$ . Volatilisation of  $\text{NaNO}_3$  and  $\text{KNO}_3$  or other volatile species from the melt was attributed as the main reason for the weight losses from the melt.
- Addition of carbonate,  $\text{Na}_2\text{CO}_3$ - $\text{K}_2\text{CO}_3$ , to the reference melt appeared to increase the thermal stability and reduce volatility during heating to 1000°C. However this stability varied with heating rate, and under thermal equilibrium conditions at 700-750°C, the carbonate containing melts lost weight at the same rate as the reference melt. This also suggests that the thermodynamic activities of the nitrate salt were not greatly decreased by the carbonate addition.

These results indicate that although the decomposition of the nitrate salt to  $\text{NO}_x$  at temperatures above  $700^\circ\text{C}$  is not a major contribution to weight loss, the molten salt will still not be stable enough for long term use as a heat transfer/storage fluid. Furthermore, the volatility of the salt at these temperatures will present an operational challenge.

### Acknowledgement

The authors wish to acknowledge helpful discussions held with colleagues at CSIRO Energy Technology in relation to this work, in particular Dr Greg Duffy,. The financial support provided by the Australian Solar Institute and the NSW Science Leveraging Fund are greatly appreciated.

### References

- [1] A. Gil, M. Medrano, I. Martorell, A. Lazaro, P. Dolado, B. Zalba, L.F. Cabeza. State of the Art on High Temperature Thermal Energy Storage for Power Generation. Part 1—Concepts, materials and modellization. *Renewable and Sustainable Energy Reviews*, 2010, 14, p31-55.
- [2] M. Medrano, A. Gil, I. Martorell, X. Potau, L.F. Cabeza. State of the Art on High Temperature Thermal Energy Storage for Power Generation. Part 2—Case studies. *Renewable and Sustainable Energy Reviews*, 2010, 14, p56-72.
- [3] M. Kenisarin. High-temperature Phase Change Materials for Thermal Energy Storage. *Renewable and Sustainable Energy Reviews*, 2010, 14, p955-970.
- [4] N. Ren, Y-t. Wu, T. Wang, C-f. Ma. Experimental Study on Optimized Composition of Mixed Carbonate for Phase Change Thermal Storage in Solar Thermal Power Plant. *Journal of Thermal Analysis and Calorimetry*, 2011, 104, p.1201–1208.
- [5] R.W. Bradshaw, C.E. Tyner. Chemical and Engineering Factors Affecting Solar Central Receiver Applications of Ternary Molten Salts. *1988 Summer National Meeting*, American Institute of Chemical Engineering, Denver, Colorado, U.S.:AIChE, 1988.
- [6] R.W. Bradshaw, D.E. Meeker. High-temperature stability of ternary nitrate molten salts for solar thermal energy systems. *Solar Energy Materials*, 1990, 21, p51-60.
- [7] R.W. Bradshaw, N.P. Siegel. Molten Nitrate Salt Development for Thermal Energy Storage in Parabolic Trough Solar Power Systems. *Energy Sustainability 2008. ES2008*, 2008, Jacksonville, Florida, 4p.
- [8] R. Olivares, Effect of Atmosphere on the Thermal Stability of Molten Nitrite/Nitrate based Salt for Solar Thermal Energy Storage. MANUSCRIPT- SE-D-11-00608, submitted to *Solar Energy Journal*, 2011.
- [9] C.M. Kramer, C.J. Wilson. The phase diagram of  $\text{NaNO}_3\text{-KNO}_3$ . *Thermochimica Acta*, 1980, 42,p253-264.
- [10] E.M. Levin, C.R. Robbins, H.F. McMurdie. *Phase diagrams for ceramists American Ceramic Society*, 1964, American Ceramic Society, Columbus, Ohio..
- [11] *Report on Operation and Maintenance Procedures for Hitec Molten Salt*, Badger Energy, Inc., Sandia National Laboratories contractor report, SAND81-8179, 1981, January, p44-46.
- [12] *Manufacture, Distribution, and Handling of Nitrate Salts for Solar Thermal Applications*, Olin Corp., Sandia National Laboratories contractor report, SAND81-8186, 1982, November, p91-92.

- [13] J.W. Raade, D. Padowitz.. Development of molten salt heat transfer fluid with low melting point and high thermal stability. *SolarPACES 2010*, 2010, p8.
- [14] J.G., Cordaro, N.C. Rubin. Multi-component molten salt mixtures based on nitrate/nitrite anions. *SolarPACES 2010*, 2010, p7.
- [15] J.G. Cordaro, A. M. Kruienza, R. Altmaier, M. Sampson, A. Nissen. Thermodynamic properties of molten nitrate salts. *SolarPACES 2011*, 2010, p8
- [16] P. Qiang, J.Ding, X. Wei, J. Yang, X.Yang, The preparation and properties of multi-component molten salts. *Applied Energy*, 2010, 87, p. 2812–2817.
- [17] R.W. Bradshaw, D A Brosseau, 2009. Sandia Corporation Patent: WO2008/071205
- [18] L. Zhang, S.Jahanshahi, S. Sun, C. Chen, B. Bourke, S. Wright, M.A. Somerville. CSIRO's Multi-Phase Reaction Model and Its Applications in Industry. *Journal of Metals*, 2002, 54, p.51-56.
- [19] H. Gaye, J. Welfringer, *The Second International Symposium on Metallurgical Slags and Fluxes*, 1984, TMMS, Warrendale, p357.
- [20] L.P. Cook, H.F. McMurdie, *Phase Diagrams for Ceramists vol VII.*, 1989, The American Ceramic Society, Inc.,
- [21] I. Ansara and B. Sundman, in *Computer Handling and Dissemination of Data*, ed. P.S. Glaser (Elsevier Science Ltd. 1986), 154-158.
- [22] R. Olivares, CSIRO-CET internal report
- [23] D.A. Nissen, D.E. Meeker. Nitrate/nitrite chemistry in sodium nitrate-potassium nitrate melts. *Inorg. Chem.*, 1983, 22(5), p716-721.
- [24] S. Gordon and C. Campbell. Differential thermal analysis of inorganic compounds nitrates and perchlorates of the alkali and alkaline earth groups and their subgroups. *Analytical Chemistry* 1955; 27(7), pp.1102-1109