

Preliminary development of thermal stability criterion for alkali nitrates

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Abstract

Development of next generation heat transfer fluids is needed to improve the performance and economics of concentrated solar power generation. Molten nitrate salts are currently used in solar power facilities, with the possibility of expanding the operating parameters to higher temperatures. Determination and understanding the maximum allowable salt temperature are of interest as this temperature range limits plant operation. Initial work combines analytical chemistry, mass loss analysis, evolved gaseous products, and remaining liquid decomposition products to aid in identifying the stability range of salt mixtures.

1. Introduction

Molten nitrite salts are currently being investigated as promising heat transfer fluids (HTFs) for concentrated solar power (CSP) applications, specifically in central receiver plants. Inherent advantages to using salts are realized by increasing the operating temperature, which is currently limited to <400°C by organic oils, thereby increasing cycle efficiency and lowering the levelized cost of electricity (LCOE) [1]. However, as proposed power cycles require an increase in the upper working temperature of the HTF, stability limitations of nitrate salts has emerged as a critical issue. Stability of salts has been generally ambiguous, with many authors investigating a variety of possible criteria that could characterize stability. This work seeks to evaluate and contrast several methods that are being considered as metrics to characterize thermal stability at high temperatures in molten nitrate and nitrite salts.

Previous efforts to understand decomposition in salts have focused on sodium nitrate over a range of temperatures and cover gases [2, 3]. The general results of these studies indicated that sodium nitrate tends to decompose rapidly above 600°C, with widespread agreement that the final product is sodium oxide [2-4]. In a practical CSP system the use of a single component molten salt is unlikely, due to the high melting point (>300°C), whereas a binary mixture of potassium nitrate and sodium nitrate reduces the melting temperature to nearly 220°C. It is of interest to determine the high temperature stability of the unary nitrates, as it is expected cation ratio will influence this parameter, and expand this to binary systems [4, 5].

Insight into chemical reaction pathways was approached by two distinct methodologies: thermo-gravimetric analysis (TGA), where the mass of a sample is monitored versus time and temperature [2, 3] and by direct analysis of the salt product [6]. Inherent advantages and disadvantages are present with both methodologies.

TGA can provide kinetic information based on heating rates. Additionally, coupling mass spectroscopy to the effluent line offers information on the volatile decomposition products. Sample size can be relatively small, on the order of milligrams, with experiment times on the order of hours, resulting in rapid screening of salt mixtures. Unfortunately, there are several limitations associated with this method.

First, the assumptions are that the reaction pathways are known and that a single reaction is dominant. The decomposition pathway of nitrates is unclear, evidenced by speculation in literature, and it is unclear that one reaction solely accounts for decomposition [2, 3, 5, 6]. That reaction pathway is nitrite and nitrate decomposing in multiple steps to form a metal oxide. It is necessary to first understand the reaction pathways then to use this information in kinetic modeling.

The second limitation encountered with the TGA method relates to the behavior of nitrate salts. Nitrate salts slowly condense on the TGA arm after repeated measurements. Great care was taken to ensure the arm was free of residual salt through various screening and cleaning processes. It is unclear if this limitation is applicable for all TGA or if it is specific to the instrument being used, as some TGA instruments employ a hanging balance vs. an arm. Chemical analysis of the salt is able to compliment and provide some insight in addition to information provided by TGA.

Direct salt sampling provides information from analysis of the evolved products. Analytical techniques can then be used for determination of nitrate decomposition products, or impurities, such as nitrites, oxides and carbonates [5, 6]. In addition to sample sizes on the order of hundreds of grams, the primary drawback to

this methodology is duration per experiment, which can last for weeks to months, depending on the setup, system, and scope.

2. Experimental Methods and Data Reduction

Pure salts were acquired from commercial sources; NaNO_3 (Riedel-de-Haen), and KNO_3 (Fisher Scientific). Prior to use, salts were dried in an oven at 250°C under a flow of nitrogen gas. Samples were weighted accurately using a 5-digit scale to ± 0.05 mg, then placed in a $40\ \mu\text{L}$ aluminum crucible and hermetically sealed. Samples (<10 mg) were heated at $20^\circ\text{C}/\text{min}$ from 50°C to the desired isothermal temperature. Figure 1 is a representative curve, showing essentially no mass loss during the initial temperature increase while significant mass loss occurs during the dwell time at fixed temperature. Four to six samples were used to obtain linear fits using the Arrhenius equation:

$$k = Ae^{-E_a/RT} \quad (1)$$

where k is the rate constant, A is the frequency factor, T is temperature (in Kelvin), R is the universal gas constant and E_a is the activation energy. Rearranging equation (1) after taking the natural log of both sides gives the following expression (Equation 2). The activation energy can be obtained by taking the natural log of each side, plotting $\ln(k)$ vs. $1/T$ and determining the slope as shown below:

$$\ln(k) = \frac{-E_a}{RT} + B \quad (2)$$

Once at the isothermal temperature, the mass loss over the first ~ 2000 seconds remains linear and pseudo-first order kinetics can be assumed. Therefore, a plot of $\ln(k)$ versus $1/T$ gives a linear plot in which the slope of the fit is E_a/R and the y-intercept is $\ln(A)$. Figure 2 represents the data reduction procedure for obtaining the rate constant. A larger E_a signifies slower decomposition rates, and hence higher kinetic stability. A nitrate salt with a larger E_a will therefore be more stable to higher temperatures.

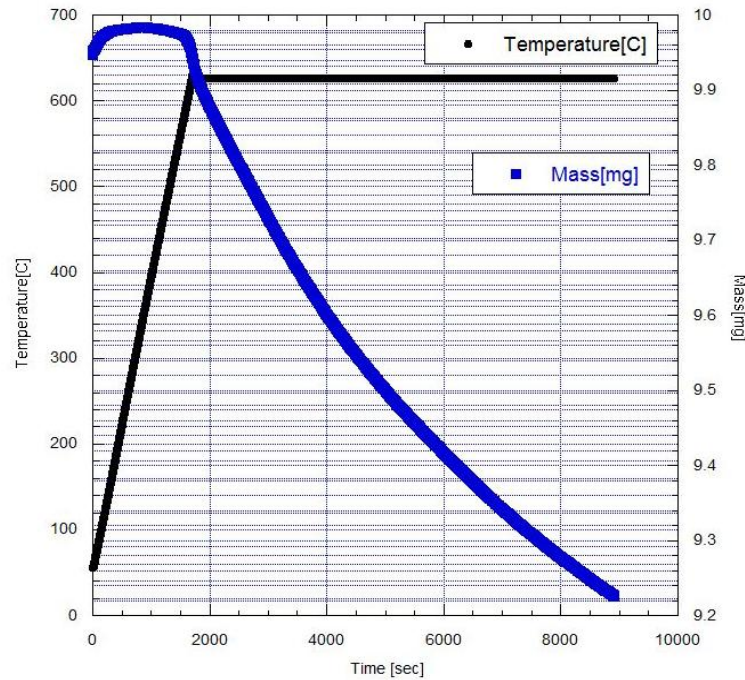
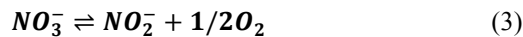


Figure 1: Sodium nitrate mass loss versus time at 625°C under an argon atmosphere.

The second metric currently being investigated for stability characterization is the presence of various ions, such as nitrite (NO_2^-) and oxides, at elevated temperatures. The equilibrium condition between nitrate (NO_3^-) and nitrite (NO_2^-) versus temperature has been determined for a 1:1 molar $\text{NaNO}_3\text{:KNO}_3$ salt, when considering the following reaction:



The equilibrium constant (K_{eq}) between nitrate, nitrite and oxygen is as follows:

$$K_{eq} = \frac{[NO_3^-]}{[NO_2^-]} P_{O_2}^{-1/2} \quad (4)$$

where P_{O_2} is the partial pressure of oxygen and values within brackets are concentration. K_{eq} has an exponential dependence temperature as:

$$K = e^{(-\Delta G^0/RT)} \quad (5)$$

where ΔG^0 is Gibb's free energy of reaction, which has been determined experimentally (reported in cal/mol) [6]:

$$\Delta G^0 = -23029 + 20.64T \quad (6)$$

Furthermore, it has been shown that standard solar salt (60:40 wt% $NaNO_3/KNO_3$) and a ternary nitrate eutectic mixture with Li, Na and K cations, closely follow the correlation developed for the equimolar binary mixture [5].

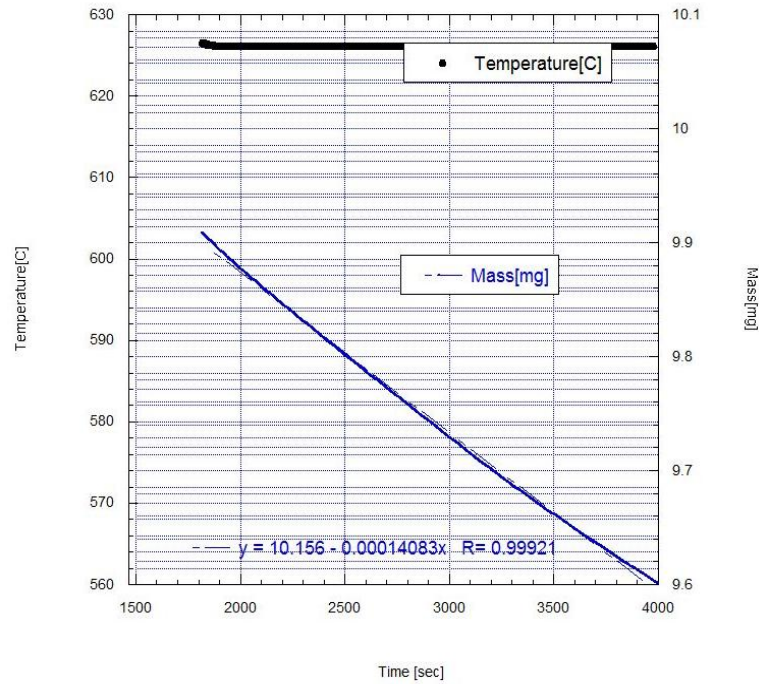


Figure 2: Initial decomposition of nitrate salt used to approximate rate. Only the linear part of the curve is used to approximate first-order kinetics.

The nitrate:nitrite ratio for two binary salt mixtures under one atmosphere of oxygen was determined from 350 – 700 °C. Mixtures both low and high potassium concentrations were tested to determine whether the equilibrium constant was affected by the cation. The extended temperature range was chosen for two purposes: first, to test whether an atmosphere of oxygen would improve the thermal stability of the salt compared to air and second, to determine if the cation concentration had an effect on the anion concentration.

Approximately 400 g of salt were contained in an alumina crucible, which was enclosed in a 316ss pressure vessel. The entire vessel was heated using an electric furnace (Figure 3). The furnace was held at temperature for approximately 48 hours prior to sampling to ensure equilibrium has been reached. Sample aliquots were taken for five consecutive days for analysis. Aliquots were drawn out of the salt pot by rapidly inserting a stainless steel rod into the molten salt and removing it so that a small portion (< 200 mg) solidified on the cold metal. The solidified salt was then added to a known amount of water and the total mass measured to determine the weight of salt. Analysis of nitrite content was performed on a spectrophotometer (Hach – DR3900) using Method 8153, as provided by the company.

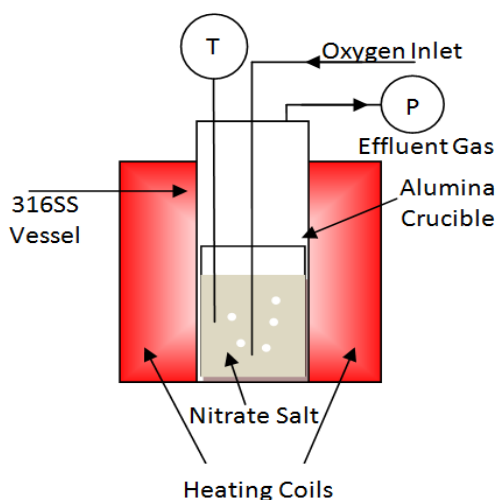
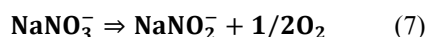


Figure 3: Large salt pot for long-term stability measurements. Typical sample size is 400 g of salt

3. Results

The initial rate of reaction for the thermal decomposition of NaNO_3 was measured at four different temperatures. These data were used to calculate an activation energy of 185.9 kJ/mol , as shown in Figure 4. This value is comparable to previous literature values of 187.1 and 168.7 kJ/mol [2, 3]. The assumed decomposition pathway for this reaction is shown in equation 7:



Mass spectroscopy data collected during the initial isothermal decomposition of NaNO_3 show a large increase for signals with $m/z = 30$ and 32 atomic mass units (amu). These ions correspond to nitric oxide (NO) and O_2 (Figure 5). This observation provides credibility to the assumed decomposition pathway in Equation 7, given the additional oxygen increase. However, it is unclear what reaction pathway gives rise to NO formation - an on-going source of speculation in the literature [2, 3, 7]. The lack of NO or any other NO_x species in previous studies could be due to low sensitivity of the equipment or different experimental conditions. In these experiments, NO was detected at five orders of magnitude lower in concentration than the argon cover gas (Figure 5). Due to the nature of the experimental setup only relative concentrations of gas content are ascertained. Other NO_x type gases could evolve during the thermal decomposition of sodium nitrate but detection is limited by competing chemical reactions in the gas phase.

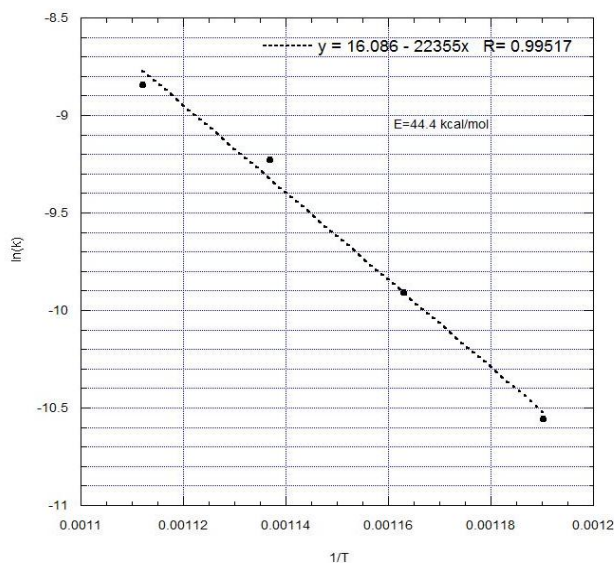
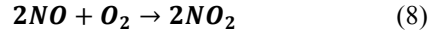


Figure 4: Plot of $\ln(k)$ vs. $1/T$ for sodium nitrate

Mass spectroscopy data were also obtained at discrete time intervals during large salt pot tests. The purpose of these experiments was to compare off-gas products obtained during TGA tests, using milligram sized samples, as representative of larger mass, hence comparing free surface to volume ratio effects. Figure 6 shows that NO was evolved as a function of time and temperature. The primary difference in these experimental set-ups is that oxygen serves as the cover gas during the large-scale salt pot study. It is interesting to note the signal corresponding to nitrogen dioxide (NO_2) with $m/z^+ = 46$, as this species was not observed in the TGA experiments under an argon atmosphere. It is likely that in an oxygen atmosphere nitric oxide is in equilibrium with NO_2 according to the following equation:



As suggested by earlier data, the equimolar nitrate/nitrite fit by Nissen predicts the ratio in the salt within the scatter of the data, independent of the cation concentration [5,8]. This fit was developed up to 620°C, and with the results of these data, the extrapolation of the equation up to 700 °C is confirmed in Figure 7. The equilibrium behavior of nitrate and nitrite appear to remain relatively constant in time, a result consistent with previous work [8], indicating the kinetic behavior of decomposition to gaseous products is possibly slower than the forward/backward evolution of nitrate/nitrite. This indicates that the fit developed by Nissen can be extrapolated to at least 700°C, in spite of the obvious decomposition of the salt as shown by the mass loss in TGA and decomposition products in the effluent stream.

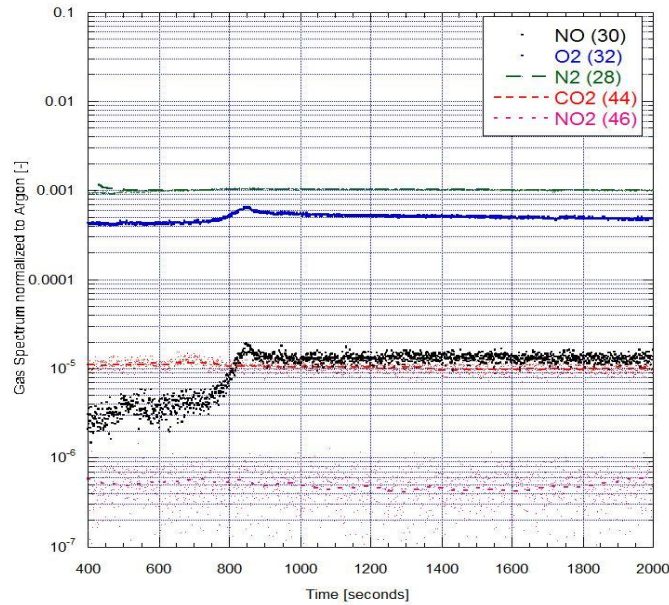


Figure 5: Relative concentration of gas detected (argon is primary cover gas, with salt at 625°C)

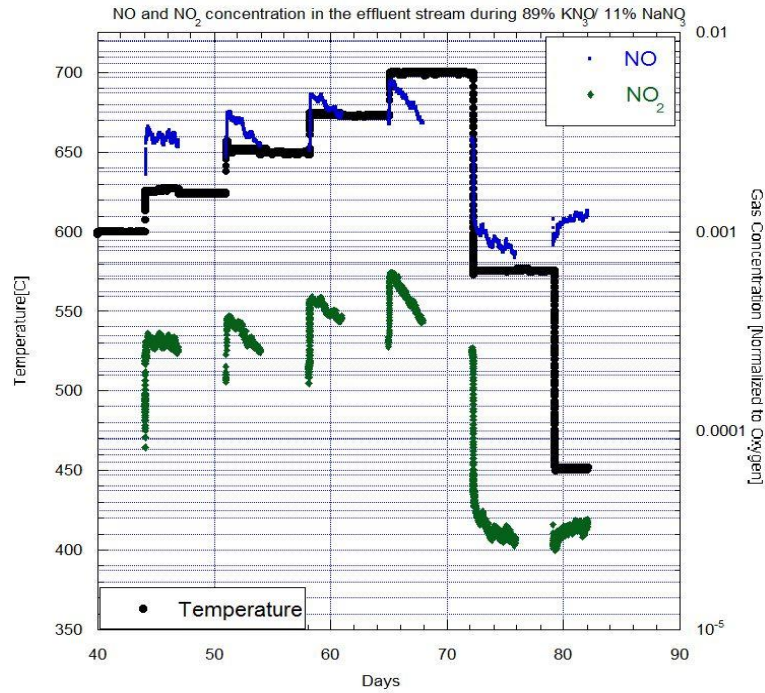


Figure 6: Mass spectroscopy signals for NO_x species versus temperature (right). Increase in relative NO_x ions corresponds to increasing temperature plotted on left.

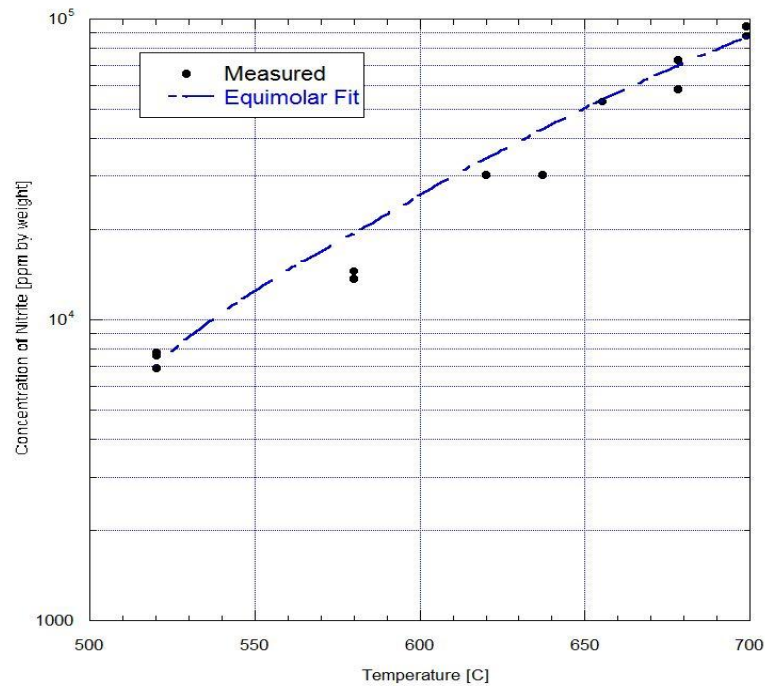


Figure 7: Nitrite concentration in 60:40 solar salt vs. temperature

4. Conclusions

Initial results of this study indicate that procedure employed to determine the activation energy of different salts is consistent with previous studies. This procedure will be employed in future studies to provide an experimental basis for determining kinetic stability. Using mass spectroscopy as a detection tool, decomposition products of O₂ and NO were observed. NO evolution is dependent upon temperature and is coupled to the Arrhenius behavior of the decomposition with higher temperatures. NO₂ was detected in the

effluent stream from salt pots, but is likely an oxidization of NO by the oxygen environment. No significant difference in the equilibrium constant was observed for different cation concentrations or under an oxygen atmosphere.

The equilibrium behavior between NO₃ and NO₂, which was fit using data gathered between 500-620°C, was found to describe data up to 700°C.

Acknowledgements

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