EQUILIBRIUM CONSTANTS OF THE NITRATE/NITRITE/OXYGEN REACTION IN MOLTEN TERNARY NITRATE SALTS MIXTURES

R. W. Bradshaw and D. E. Meeker
Sandia National Laboratories
Livermore, CA 94551-0969

ABSTRACT

We have evaluated the chemical equilibria of the decomposition reactions of ternary mixtures of molten nitrate salts consisting of sodium and potassium nitrate with additions of either calcium, barium or lithium nitrate. The equilibrium constant of the initial reaction, nitrate = nitrite + oxygen, was relatively insensitive to the composition of the mixtures. The extent to which subsequent decomposition reactions proceeded was dependent on the type and amount of the additions to the binary alkali nitrate mixture and was related to the charge and size of the added cationic species.

Introduction

Ternary mixtures of NaN0₃ and KNO₃ with other alkali and alkaline earth nitrates have much lower melting points than the binary alkali salt mixture (equimolar, m.p. 238°C). For example, the eutectic of LiNO₃, NaN0₃, and KNO₃ (30:18:53, wt.%) melts at 120°C, while the mixture 30 Ca(NO₃)₂-24 NaN0₃-46 KNO₃ (wt.%) melts at approximately 160°C [1]. Salt mixtures with lower melting points have potential applications as energy collection and storage fluids in advanced solar thermal energy systems [2].

The chemical equilibrium of the binary alkali mixture has been studied at high temperature and the mixture is quite stable, in the presence of oxygen, up to 600°C [4]. The stability of ternary mixtures containing calcium or lithium nitrate additions is expected to be less than that of the binary mixture because pure Ca(NO₃)₂ and LiNO₃ are less stable at high temperature than NaN0₃ and KNO₃ [5]. No quantitative measurements of the equilibria of mixtures containing calcium or lithium nitrate appear to have been made, although some incidental observations of decomposition of mixtures of Ca(NO₃)₂ and KNO₃ [6,7,8] and a mixture of Li/Na/K/NO₃ [9] have been reported.

The purpose of this study was to evaluate the chemical stability of ternary mixtures of alkali and alkaline earth nitrates. The approach taken was to determine the extent of decomposition, with respect to the formation of nitrate and oxide ions, of oxygen-saturated, ternary salt
mixtures at equilibrium. Experiments were conducted with mixtures of 
Li/Na/K/NO₃, Ca/Na/K/NO₃ and Ba/Na/K/NO₃.

EXPERIMENTAL

The ternary nitrate mixtures were prepared from reagent grade 
salts without further purification. Melts were allowed to equilibrate 
for at least 48 hours after establishing the temperature of each 
experiment. Several samples of salt were withdrawn, using a quartz 
pipet, at various times during the next 24 hours or more, which was 
sufficient to attain constant composition. The temperature of a given 
mixture was raised in increments until insoluble decomposition products 
were observed or a temperature of 600°C was reached. The details of the 
experimental procedure can be found in Ref. [3].

Melts containing lithium nitrate were studied using the apparatus 
described by Nissen and Meeker [4]. Salt mixtures were prepared in a 
glove box to avoid water absorption by LiNO₃. The melts were contained 
in platinum crucibles, enclosed within a hermetically-sealed vessel, 
and were sparged with oxygen at one atmosphere total pressure. This 
apparatus had a provision for removing traces of carbon dioxide from 
the inlet gas stream, which eliminated the possibility of reactions 
between CO₂ and oxide ions formed in the melt.

Experiments with melts containing alkaline earth nitrates were 
conducted in a furnace open to the atmosphere. Mixtures totaling 300 to 
400 grams were melted in aluminum oxide crucibles. Water was readily 
evolved from the salts upon melting, with visual indications ceasing 
after a few hours. The melts were sparged with air from the laboratory 
compressed air supply at a rate of 100-200 sccm. Air was passed through 
a Drierite (calcium sulfate) column to dry and filter it before 
bubbling through the melt. CO₂ was not removed from the inlet gas 
stream. A small amount (<0.03 wt.%) of a reddish-brown precipitate, 
apparently derived from calcium nitrate, formed upon heating to about 
300°C. The insoluble material was filtered out by passing the melt 
through Pyrex-glass wool, after which the melts became water-clear. The 
residue was analyzed by X-ray diffraction and infrared spectroscopy and 
found to consist of CaO and a silicate.

RESULTS AND DISCUSSION

The equilibrium chemistry of molten nitrate salts has been 
reviewed elsewhere [10,11]. Metal nitrates decompose to yield the 
corresponding nitrite in equilibrium with the ambient oxygen activity, 
according to Eq. 1.

\[
\text{NO}_3^- = \text{NO}_2^- + \frac{1}{2} \text{O}_2
\]

The equilibrium constant for the above reaction, \( K_1 \), is given by
where the molal concentrations of the anions and the partial pressure of oxygen are substituted for the activities of the compounds.

Nitrite, formed by Eq. 1, and nitrate may subsequently decompose to yield various oxide ion species (oxide, peroxide, and superoxide). The equilibrium chemistry of oxide ions in nitrate/nitrite melts is rather complicated and somewhat controversial [10,11]. Common impurities, such as water vapor and carbon dioxide, which behave as Lux-Flood acids in these melts, have marked effects on the concentrations of oxide ion species in nitrate melts [10,11]. For example, the carbon dioxide in air may convert oxide ion species to carbonate,

\[
\text{(3)} \quad \text{CO}_2 + \text{O}^{--} = \text{CO}_3^{--}
\]

In this study, the decomposition behavior of ternary nitrate melts was characterized by the amount of nitrite ion formed and by the concentrations of oxide ions or derivative species, such as carbonate.

Lithium-Sodium-Potassium Nitrate Mixtures

A number of ternary mixtures of LiNO\textsubscript{3} with NaNO\textsubscript{3} and KNO\textsubscript{3} were studied at temperatures between 500°C and 600°C. These values of \(K_1\) were comparable to those of the binary mixture of NaNO\textsubscript{3} and KNO\textsubscript{3} over the temperature range studied, as shown in Figure 1. A small but systematic increase in \(K_1\) was observed as the mole fraction of LiNO\textsubscript{3} increased (neglecting variations in the amounts of NaNO\textsubscript{3} and KNO\textsubscript{3}). The enthalpy change of reaction 1, obtained from the slope of the Arrhenius plot, was essentially independent of composition. The average slope of the five LiNO\textsubscript{3}-containing mixtures was 22.9 kcal/mol, essentially equal to that of the binary mixture, 23.0 kcal/mol [4].

Ternary mixtures containing LiNO\textsubscript{3} formed much larger concentrations of oxide ions at high temperature than the binary mixture, which was reported to have less than 10 micromolal total oxide under these conditions [4]. The formation of oxides was very sensitive to the amount of LiNO\textsubscript{3} in the mixtures, as shown in the semi-log plot in Figure 2. Below about 40 mol.\% LiNO\textsubscript{3}, the concentration of oxide ions increased sharply as the LiNO\textsubscript{3} content increased. A further increase in LiNO\textsubscript{3} content resulted in a much smaller increase in oxide concentration. Solubility may have been limiting the amount of oxide in the melt.

The equivalent concentration of oxide ions attained a maximum value at 550°C, regardless of the initial composition. Increasing the temperature from 550°C to 600°C caused a small decrease in the total oxide concentration of all the ternary mixtures analyzed. This behavior may be due to conversion of oxide or peroxide ions to superoxide at
high temperature [14], thereby reducing the equivalent amount of
hydroxide measured during titrations by half.

Calcium-Sodium-Potassium Nitrate Mixtures

Molten salt mixtures containing calcium nitrate behaved quite
similarly to the binary alkali mixture with respect to nitrite
formation. The Arrhenius plot in Figure 3 shows values of $K_4$ for
several mixtures of Ca(NO$_3$)$_2$, NaNO$_3$, and KNO$_3$ and compares them to the
data in the literature for the binary mixture [4], NaNO$_3$ [12] and KNO$_3$
[13]. Although calcium-containing mixtures displayed slightly lower
values of $K_4$ than the binary salt, the effect of Ca(NO$_3$)$_2$ concentration
on $K_4$ was negligible over the range studied. The data for all ternary
mixtures were fitted to a single Arrhenius equation and a slope
corresponding to an enthalpy change of 16.4 kcal/mol for Eq. 1 was
obtained, somewhat less than that reported for the binary mixture, 20.3
kcal/mol [4].

The most obvious indication of decomposition at high temperature
was the formation of a solid phase. Typically, the melts were
maintained at each successively higher temperature for several days,
without discoloration or other visible deterioration, over a cumulative
period of several weeks. At the highest temperature of each experiment,
solid formation was observed. In one experiment, a mixture containing
30 mol% Ca(NO$_3$)$_2$ was kept at 462°C for more than two weeks without a
significant change in the chemical analysis or any visible changes in
the melt.

The solid phase that formed in the melts was identified as calcium
carbonate by X-ray diffraction analysis. The amount of each precipitate
was not measured but was less than a few percent of the total mass of
the melts in all experiments. The temperature at which the precipitate
appeared decreased as the concentration of Ca(NO$_3$)$_2$ increased. The
temperatures attained show that although Ca(NO$_3$)$_2$ reduces the stability
of the mixture, the reduction is not as drastic as might be expected
from the behavior of the pure salt [5].

Carbonates are formed by the reaction of carbon dioxide, in the
air passed through the melts, with oxide ions produced by decomposition
of nitrite and nitrate. No free oxide ions were detected in these
mixtures, which indicates that the equilibrium constant for Eq. 3 is
large, just as it appears to be in the binary alkali salt [15].

Barium-Sodium-Potassium Nitrate Mixtures

Equilibrium experiments were conducted with two ternary mixtures
comprised of barium nitrate in sodium/potassium nitrate. Barium-
containing mixtures were more stable than calcium-containing mixtures
at the same concentration of alkaline earth nitrate. With respect to
the nitrate-nitrite-oxygen reaction, barium-containing mixtures behaved
similarly to the binary alkali mixture, as shown by the values of $K_1$ plotted in Figure 4. The differences between mixtures in which the mole fractions of $\text{Ba(NO}_3\text{)}_2$ were 0.2 or 0.3 were quite small. The enthalpy changes for Eq. 1 for these two mixtures were 27.4 and 25.6 kcal/mol respectively, somewhat larger than the values for the binary mixture or calcium-containing ternary salts.

Decomposition of barium-containing ternary salts at high temperature produced a solid phase. This phase was not analyzed but it was assumed to be barium carbonate, since the titrimetric analysis showed carbonate but no free oxides. The temperature required to produce visible quantities of decomposition products decreased as the concentration of $\text{Ba(NO}_3\text{)}_2$ increased analogous to ternary mixtures containing $\text{Ca(NO}_3\text{)}_2$. However, the temperature required to cause decomposition was higher than for mixtures with added $\text{Ca(NO}_3\text{)}_2$ at the same mole fraction of the alkaline earth nitrate.

**Effect of Composition on Stability of Mixtures**

The trend of stability of ternary salt mixtures, as indicated by the maximum temperature at which decomposition products became appreciable, is approximately $\text{Ca} < \text{Li} < \text{Ba}$. This order is somewhat arbitrary for Li and Ba since the cover gases were not the same. Regardless of this distinction, the stability of ternary salts followed the correlation for single salts established by Stern [5]. This correlation is based upon a parameter of the cationic species consisting of the square root of the covalent metallic radius, $r$, divided by the effective nuclear charge, $Z$. Stability increases as the cation parameter increases, which implies that electrostatic effects between the cations and the polyatomic anions are important. The values of this parameter for the alkali and alkaline earth metals of interest are given below [5].

| Cation | $r^{0.5}/Z$ |
|--------|-------------|
| Ca     | 0.38        |
| Li     | 0.45        |
| Ba     | 0.46        |
| Na     | 0.53        |
| K      | 0.62        |

The stability of ternary mixtures appears to be determined primarily by the least stable constituent since the nitrates of sodium and potassium are much more stable than the other nitrates. However, molten mixtures of nitrates appeared to be more stable than the least stable individual salts. Lithium nitrate has been reported to decompose to nitrite and oxide just above its melting point of 258°C [5], but ternary mixtures of Li/Na/K/NO$_3$ were relatively stable in the presence of oxygen. Similarly, barium nitrate reportedly decomposes upon melting [5], but its mixtures were fairly stable.
The types of cations in the salt mixtures had relatively little effect on the nitrate/nitrite reaction (Eq. 1) over the range of compositions investigated. The equilibrium constants for this reaction were quite similar for all the ternary mixtures, although a systematic increase in the enthalpy change of Eq. 1 was observed in the order Ca < Li < Ba. This order follows Stern's correlation for the pure salts [5], although the relative differences in enthalpies were less for mixtures. This observation suggests that nitrate ions are surrounded by a group of cations corresponding to the composition of a given ternary mixture and that clustering of one type of cation does not occur. It is also possible that the larger sodium and potassium ions may shield nitrate ions somewhat from the smaller, more polarizable cations (Ca\(^{2+}\), Li\(^+\), Ba\(^+\)) and thereby stabilize the ternary mixtures.

In contrast, decomposition of the ternary mixtures beyond the nitrate/nitrite/oxygen reaction was strongly influenced by the types of cations present. This suggests that cations may interact with nitrite or oxide ions, which are smaller than nitrate, by clustering, rather than randomly. Clustering is a possible explanation for the marked dependence of oxide ion formation on the concentration of LiNO\(_3\) in ternary salts discussed above.

CONCLUSIONS

The high temperature chemical stability of molten mixtures of sodium and potassium nitrates were reduced somewhat by the addition of either calcium (or barium) nitrate or lithium nitrate. The ternary mixtures behaved quite similarly to binary (sodium and potassium nitrate) mixtures with regard to the nitrate/nitrite/oxygen reaction. The equilibrium constant of this reaction was relatively insensitive to the composition of the ternary salt mixtures over the range studied. Oxide ion equilibria in ternary nitrate melts appear to exert a strong influence on the formation of insoluble material, which is a limiting factor with regard to the maximum useable temperature in applications.

Acknowledgements

This work was supported by U.S. Dept. of Energy Contract DE-AC04-76DP00789. Helpful discussions with D. A. Nissen of Sandia National Laboratories were much appreciated.

References

1. Phase Diagrams for Ceramists, E. M. Levin, C. R. Robbins and H. F. McMordie, eds., Vols. I and II, Amer. Ceram. Soc., 1964.
2. R. W. Bradshaw and C. E. Tyner, "Chemical and Engineering Factors Affecting Solar Central Receiver Applications of Ternary Molten Salts", A.I.Ch.E., Summer National Meeting, Denver, CO, Reprint 90b, Aug. 1988;
3. R. W. Bradshaw and D. E. Meeker, "Chemical Equilibria of Molten Ternary Nitrate Salt Mixtures," Sandia National Laboratories, SAND88-8845, May 1989.
4. D. A. Nissen and D. E. Meeker, Inorg. Chem., 22, 716 (1983).
5. K. H. Stern, J. Phys. Chem. Ref. Data, 1 (3), 747 (1972).
6. E. Rhodes, W. E. Smith and A. R. Ubbelohde, Proc. Roy. Soc., A285, 263 (1965).
7. M. D. Ingram and G. G. Lewis, J. Electroanal. Chem., 5, 399 (1974).
8. A. A. K. Al-Mahdi, J. Appl. Chem., 14, 269 (1964).
9. R. A. Archer and B. R. Dunbobbin, "Pilot Plant Development of a Chemical Air Separation Process", Air Products and Chemicals, Inc., U.S.D.O.E. report DOE/CS/40544-T1, May 1985.
10. B. W. Hatt, in Molten Salt Technology, D. G. Lovering, ed., Plenum Press, p. 483ff, 1982.
11. J. Jordan, W. B. McCarthy and P. G. Zambonin, in Molten Salts, G. Mamantov, ed., Academic Press, p. 575ff (1969).
12. G. D. Sirotkin, Russ. J. Inorg. Chem., 4, 1180 (1959).
13. R. F. Bartholomew, J. Phys. Chem., 70, 3442 (1966).
14. D. R. Flinn and K. H. Stern, J. Electroanal. Chem., 63, 39 (1975).
15. R. N. Kust, Inorg. Chem., 3 (7), 1035 (1964).

Registry No. \( \text{NO}_3^- \), 14797-55-0; \( \text{NO}_2^- \), 14797-65-0.
\( \text{NaNO}_3 \), 7631-99-4; \( \text{KNO}_3 \), 7757-79-1; \( \text{Ca(NO}_3)_2 \), 10124-37-5;
\( \text{Ba(NO}_3)_2 \), 10022-31-8; \( \text{LiNO}_3 \), 790-69-4;
Figure 1
Arrhenius plot of the equilibrium constants of the reaction, nitrate = nitrite + oxygen, for Li/Na/K/NO₃ mixtures. The dashed line represents data from the literature for the equimolar mixture of NaNO₃ and KNO₃.

Figure 2
Semi-log plot of the equivalent oxide ion concentration of various molten Li/Na/K/NO₃ mixtures at 1 atm. O₂ pressure.
Figure 3
Arrhenius plot of the equilibrium constants of the reaction, nitrate = nitrite + oxygen, for Ca/Na/K/NO$_3$ mixtures (solid line). The broken lines represent data from the literature for the salts designated.

Figure 4
Arrhenius plot of the equilibrium constants of the reaction, nitrate = nitrite + oxygen, for Ba/Na/K/NO$_3$ mixtures.