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Pressure-Temperature-Composition Relationships For Heated Drawsalt Systems

(Submitted to *Solar Energy Materials*)

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Prepared by Sandia Laboratories, Albuquerque, New Mexico 87115
and Livermore, California 94550 for the United States Department
of Energy under Contract DE-AC04-76DP00789.

Printed December 1980

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PRESSURE-TEMPERATURE-COMPOSITION RELATIONSHIPS
FOR HEATED DRAWSALT SYSTEMS

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ABSTRACT

A molten nitrate salt mixture consisting of 60% NaNO_3 and 40% KNO_3 by weight is an attractive candidate for a heat transfer and thermal energy storage fluid in large-power solar systems. The relationships between pressure, temperature, and composition (nitrate to nitrite ratio) have been determined for this salt mixture under two system configurations: constant volume (sealed containment) and constant pressure (open containment). For the first, families of pressure-temperature and composition-temperature curves were generated for initial salt volume fractions of 0.1 to 0.7. For the constant pressure system, composition-temperature curves were generated for oxygen pressures of 1, 0.2, 0.01, and 0.001 atm.

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PRESSURE-TEMPERATURE-COMPOSITION RELATIONSHIPS FOR HEATED DRAWSALT SYSTEMS

Introduction

Nitrate salts have been proposed for use in solar thermal energy systems as a heat transfer fluid and thermal energy storage medium, and numerous systems using nitrates are in various stages of design and development.¹ The salt composition with the greatest industrial use is a ternary mixture of 40% NaNO_2 , 7% NaNO_3 , and 53% KNO_3 by weight. This mixture is marketed by Coastal Chemical under the trade name HITEC and by Park Chemical Company under the trade name PARTHERM 290.

Studies have shown the ternary composition to be unsuitable for use in solar large power systems.² Rather, interest has centered on drawsalt,² which is nominally an equimolar eutectic mixture of NaNO_3 and KNO_3 . In applications calling for copious quantities of salt, a significant cost savings can be realized by using an off-eutectic mixture containing an excess of NaNO_3 , the less costly component. A NaNO_3 -rich mixture containing 60% NaNO_3 and 40% KNO_3 by weight is commercially marketed by Park Chemical Company under the trade name PARTHERM 430. This study examines the behavior of such a salt. The relationships between pressure, temperature, and composition (nitrite to nitrate level) are analyzed under several different conditions pertinent to large-power solar systems.

In preliminary design studies^{2,3} the salts have been allowed to communicate freely with the atmosphere. However, it is well known that nitrates interact with H_2O and CO_2 to form hydroxides and carbonates.⁴ Over extended periods of operation the fluid may degrade significantly because of hydroxide and carbonate formation. One alternative approach is to force the system to "breathe" through a scrubbing system that removes the H_2O and CO_2 before they can form hydroxides and carbonates. A nonreactive cover gas may also inhibit deleterious interactions. In both cases, the system operates as a fixed pressure system. Another solution is to completely seal the salt from the atmosphere. In this case the system operates as a fixed-volume system.

When a nitrate salt is heated, partial decomposition is inevitable. From an initially pure nitrate composition a mixture of nitrate and nitrite evolves. The ultimate salt composition (nitrate-to-nitrite ratio) depends upon the pressure and composition of the cover gas and the temperature. The relationships between pressure, temperature, and salt composition under the two conditions of fixed volume and fixed pressure are examined here.

Background

The nitrates of sodium, potassium, and their mixtures melt without decomposing significantly.⁵ Continued heating to higher temperatures causes the nitrate to decompose by a variety of reaction paths.⁶⁻¹⁰ The principal decomposition reaction is



where M is Na, K, or a mixture thereof, as shown by Buchler and Stauffer's¹¹ study of $NaNO_3$ and by Freeman's⁷ studies of $NaNO_3$ and KNO_3 . Nitrogen appears at temperatures greater than $700^\circ C$.^{5,6}

Other secondary decomposition reactions have been observed or hypothesized, including direct vaporization to form complex nitrate gas species¹¹⁻¹³ and the formation of oxides in the melt with the release of N_2 and NO_2 .^{8,9} These reactions are favored by high temperature ($> 700^\circ C$) and continual gas product removal, as under evacuated conditions. Neither of these conditions should exist in an operating solar-energy power plant. It has also been suggested that secondary decomposition reactions are more directly a result of corrosion reactions with containment materials.¹⁴ Therefore, it is assumed in this study that secondary decomposition reactions are unimportant and that Eq. (1) is a complete and adequate representation of the chemistry within a container filled with nitrate salt.

It is informative to apply the phase rule to the problem at hand. Upon heating a mass of nitrate salt, a portion of it decomposes to form oxygen and nitrite according to Reaction (1), the oxygen being liberated as a gas and the nitrite forming a liquid solution with the remaining nitrate. There are thus two phases present in a sealed system, the gas phase and the liquid solution, and there are two independent components, the nitrate and the nitrite. From the phase rule

$$F = C - P + 2 \quad (2)$$

for P phases, C independent components, and F degrees of freedom, it is seen that there are two degrees of freedom. Therefore, one cannot define a unique pressure by specifying a temperature alone; a singular pressure is defined only if an additional degree of freedom is consumed. This extra degree of freedom was specified in this study by two methods. In one, volume constraints were imposed; in other words, the starting volume fraction of the salt and the container volume were specified. In the other, we considered the pressure to be fixed along with the temperature, thereby fixing the salt composition.

Sealed Containment Systems

Mathematical Analysis

Initially, one is given a container of volume V_T containing a given amount of salt. The initial conditions are specified by one parameter, a , the initial salt volume fraction. Upon heating, the nitrate salt partially decomposes, and the salt reaches a final composition of $X_{NO_2^-}$ and $X_{NO_3^-}$ mole fractions of nitrite and nitrate, respectively. The system pressure is at P_{O_2} .

The basic working relationship for this analysis is

$$\Delta G_T^0 = -RT \ln \left(\frac{P_{O_2}^{1/2} X_{NO_2^-}}{X_{NO_3^-}} \right), \quad (3)$$

which is derived from a thermodynamic analysis of Eq. (1) assuming ideal solution behavior. The strategy is to modify Eq. (3) so that the only variables are the final nitrite concentration $X_{NO_2^-}$, the initial salt volume fraction a , and the temperature T . From such an expression, one can solve for $X_{NO_2^-}$ given a and T .

Assuming ideal-gas conditions exist, one can express the oxygen pressure P_{O_2} as

$$P_{O_2} = \frac{N_{O_2} RT}{V_g} \quad (4)$$

where N_{O_2} is the number of moles of oxygen in the gas phase and V_g is the volume of the gas phase. The gas volume is calculated from

$$V_g = V_T - V_S \quad (5)$$

where V_T is the constant total volume of the system and V_S is the volume of the molten salt. V_T can be expressed as a function of parameters defining the initial system:

$$V_T = \frac{N_{NO_3^-}^i w_{NO_3^-}}{a \rho_s} \quad (6)$$

where $N_{NO_3^-}^i$ is the initial number of moles of nitrate, $w_{NO_3^-}$ is the molecular weight and ρ_s is the room-temperature density of the salt in solid form. The density of a molten mixture of nitrate-nitrite is commonly expressed in the form

$$\rho_l = a + bT + cX_{NO_2^-} \quad (7)$$

where ρ_l is the molten salt density expressed in units of g/cm^3 and a , b , and c are constants.¹⁴ The molten salt volume V_S can thus be represented as

$$V_S = \frac{W_{\text{NO}_3^-} N_{\text{NO}_3^-} + W_{\text{NO}_2^-} N_{\text{NO}_2^-}}{a + bT + cX_{\text{NO}_2^-}} \quad (8)$$

where $W_{\text{NO}_3^-}$ and $W_{\text{NO}_2^-}$ are the molecular weights of the nitrate and nitrite mixture, respectively, and $N_{\text{NO}_3^-}$ and $N_{\text{NO}_2^-}$ are the moles of nitrate and nitrite.

Expressing $N_{\text{NO}_3^-}$ and $N_{\text{NO}_2^-}$ in terms of $X_{\text{NO}_2^-}$ and $N_{\text{NO}_3^-}^i$, reaction stoichiometry requires that

$$N_{\text{NO}_3^-} = N_{\text{NO}_3^-}^i - N_{\text{NO}_2^-} \quad (9)$$

and

$$2N_{\text{O}_2} = N_{\text{NO}_2^-} \quad (10)$$

But since

$$X_{\text{NO}_2^-} = \frac{N_{\text{NO}_2^-}}{N_{\text{NO}_3^-} + N_{\text{NO}_2^-}}$$

it follows that

$$X_{\text{NO}_2^-} = \frac{N_{\text{NO}_2^-}}{N_{\text{NO}_3^-}^i} \quad (11)$$

and therefore,

$$N_{\text{NO}_2^-} = N_{\text{NO}_3^-}^i X_{\text{NO}_2^-} \quad (12)$$

Similarly, for $N_{\text{NO}_3^-}$ one has

$$N_{\text{NO}_3^-} = N_{\text{NO}_3^-}^i (1 - X_{\text{NO}_2^-}) \quad (13)$$

Substituting terms into Eq. (4) and simplifying leads to the following:

$$P_{O_2} = \frac{X_{NO_2} RT}{2 \left[\frac{W_{NO_3}}{s} - \frac{W_{NO_3}(1-X_{NO_2}) + W_{NO_2}X_{NO_2}}{a+bT+cX_{NO_2}} \right]} \quad (14)$$

Substitution into Eq. (3) gives

$$\Delta G_T^0 = -RT \ln \left\{ \frac{X_{NO_2} RT}{2 \left[\frac{W_{NO_3}}{a\rho_s} - \frac{W_{NO_3}(1-X_{NO_2}) + W_{NO_2}X_{NO_2}}{a+bT+cX_{NO_2}} \right]} \right\}^{1/2} \frac{X_{NO_2}}{1-X_{NO_2}} \quad (15)$$

In the analysis to follow, values for T and a are selected, the free energy change ΔG_T^0 is calculated from thermochemical data, and Eq. (15) is solved

numerically for X_{NO_2} . Knowing X_{NO_2} allows one to calculate the oxygen pressure by Eq. (14). In this manner families of pressure-temperature curves have been generated for varying initial salt volume fractions; composition-temperature curves have been calculated as well.

Calculated Relationships

For the calculations described above, we need values for the free energy change, the room-temperature salt density, and the fluid salt density as a function of temperature and nitrite concentration. The standard-state free energy change for the nitrate decomposition Reaction (1), where M is $Na_{0.64}K_{0.36}$, was taken to be²

$$\Delta G_T^0 \text{ (cal/mole nitrate)} = 25.3T(K) - 27540 \quad (16)$$

The room-temperature salt density was taken to be 2.198 g/cm^3 , which was estimated by a linear combination of properties for $NaNO_3$ and KNO_3 . The fluid salt density was similarly estimated from data presented by Krebs et al.¹⁵ for $NaNO_3$ and KNO_3 :

$$\rho_l \text{ (g/cm}^3\text{)} = 2.2775 - (6.58)10^{-4}T(K) - (0.108)X_{NO_2}$$

The calculated behavior for Partherm 430 is shown in Figures 1 and 2. Pressure-temperature and composition-temperature curves are given for initial salt volume fractions from 0.1 to 0.7. The calculations were limited to an upper temperature of 1000 K because above this temperature the assumption that the nitrate/nitrite reaction is the only important reaction is invalid. The pressures and nitrite concentrations are seen to increase monotonically with temperature. The temperature dependence approximately follows an Arrhenius

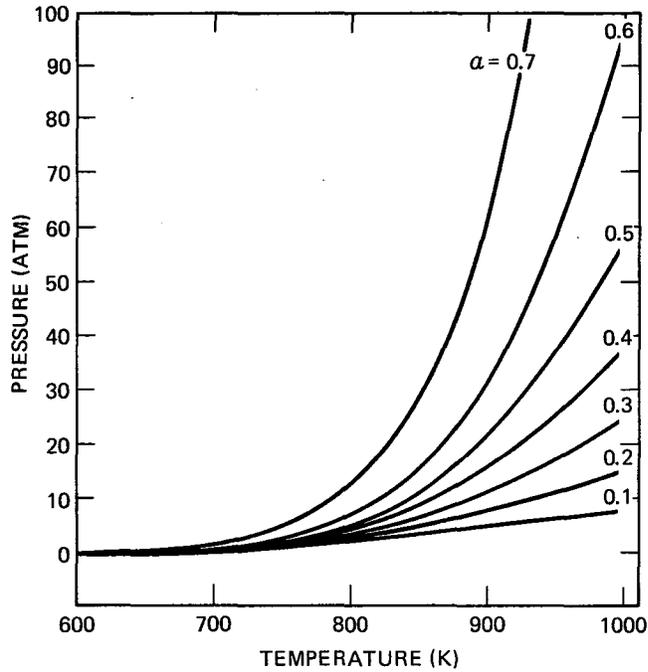


Figure 1. Pressure-Temperature Relationships for 60% NaNO₃-40% KNO₃ (by Weight) Salt Mixtures Heated in a Sealed System for Various Initial Salt Volume Fractions.

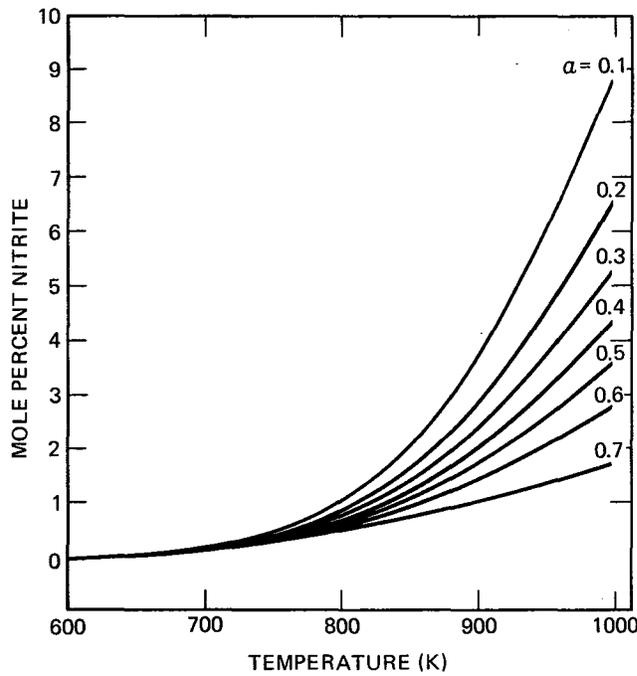


Figure 2. Composition-Temperature Relationships for 60% NaNO₃-40% KNO₃ (by Weight) Salt Mixtures Heated in a Sealed System for Various Initial Salt Volume Fractions.

relation, where the log of the pressure and log of the nitrite concentration are both proportional to the inverse of temperature.

As the system approaches overflow conditions--that is, when the salt volume approaches that of the container, thereby causing the ullage gas volume to approach zero--deviations from Arrhenius behavior are found. To illustrate these characteristics, we show in Figure 3 the behavior of a system initially filled to a volume fraction α of 0.8. It is seen that the pressure increases monotonically with temperature and that the increase is greater than predicted by an Arrhenius relationship. Overflow conditions are reached at approximately 789 K. The nitrite level is seen to reach a maximum before attaining overflow. This result is a consequence of two competing processes. At higher temperatures a greater amount of nitrate decomposes and the nitrite level increases; however, the salt also expands, reducing the gas volume and therefore reducing the amount of oxygen decomposition product that can be accommodated. We note though that under realistic conditions (reasonable initial salt fills) overflow conditions are never reached. Initial salt fill volume fractions α are generally less than 0.5.

Experimental Observations

Two experiments were conducted to verify the validity of the calculations and assumptions described above. Drawsalt of the Partherm 430 composition (60% NaNO_3 -40% KNO_3 by weight) was prepared from reagent grade NaNO_3 and KNO_3 . The salt was placed in closed-end alumina tubes which were sealed by means of compression O-ring fittings and evacuated. The tube containers were instrumented to measure the pressure continuously. Two experiments were conducted, one with an initial salt volume fraction loading of $\alpha = 0.06$ and another with $\alpha = 0.17$. The tube containers were placed in a furnace with the compression fitting placed outside of the furnace. The experimental configuration was designed so that $\approx 90\%$ of the container volume was held at the salt temperature. Therefore it is valid to compare directly the experimental results and the calculations discussed in this study, which assumed the gas and salt temperatures were the same. The temperature for both experiments was 863 K. The pressure was monitored until steady state was reached.

The results are shown in Figure 4, where the two experimental data points appear on a plot of pressure versus initial salt volume. Also shown for comparison are several calculated isotherms. There is excellent agreement between the experimentally measured pressures and those calculated.

Open Containment Systems

In an open system the nitrate salt is exposed to a constant total pressure of one atmosphere, but the oxygen partial pressure, while constant, may vary from system to system. If the oxygen partial pressure and temperature are specified, one can calculate a unique salt composition (nitrite-to-nitrate ratio) using Eqs. (3) and (16). Accordingly, composition-temperature curves have been calculated and plotted in Figure 5 for four different oxygen pressures: 1.0, 0.2, 0.01, and 0.001 atm. The 0.2-atm curve is obviously important because it

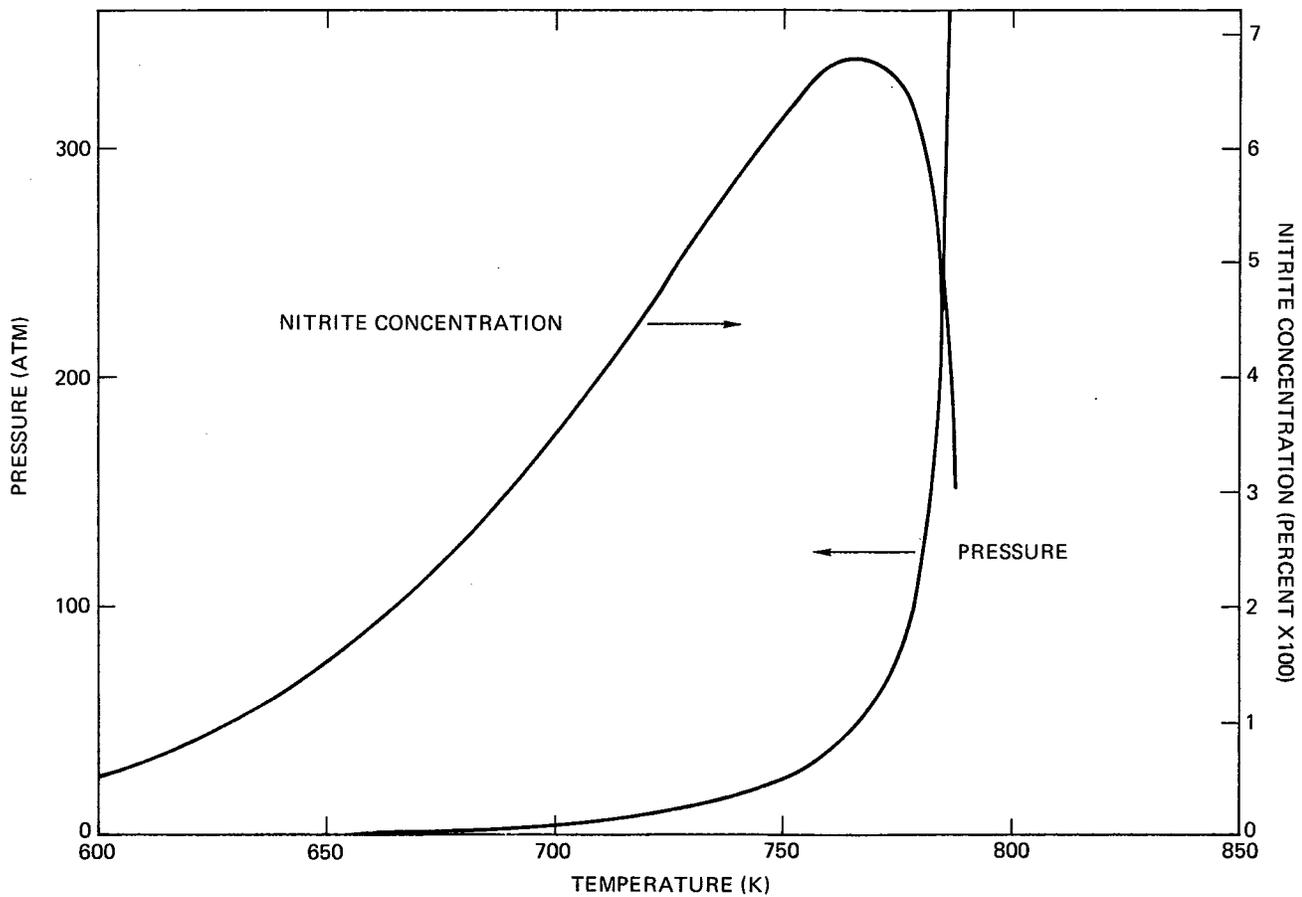


Figure 3. Behavior of a Sealed Container Filled With a 60% NaNO_3 -40% KNO_3 (by Weight) Salt Mixture to an Initial Volume Fraction of $\alpha = 0.8$.

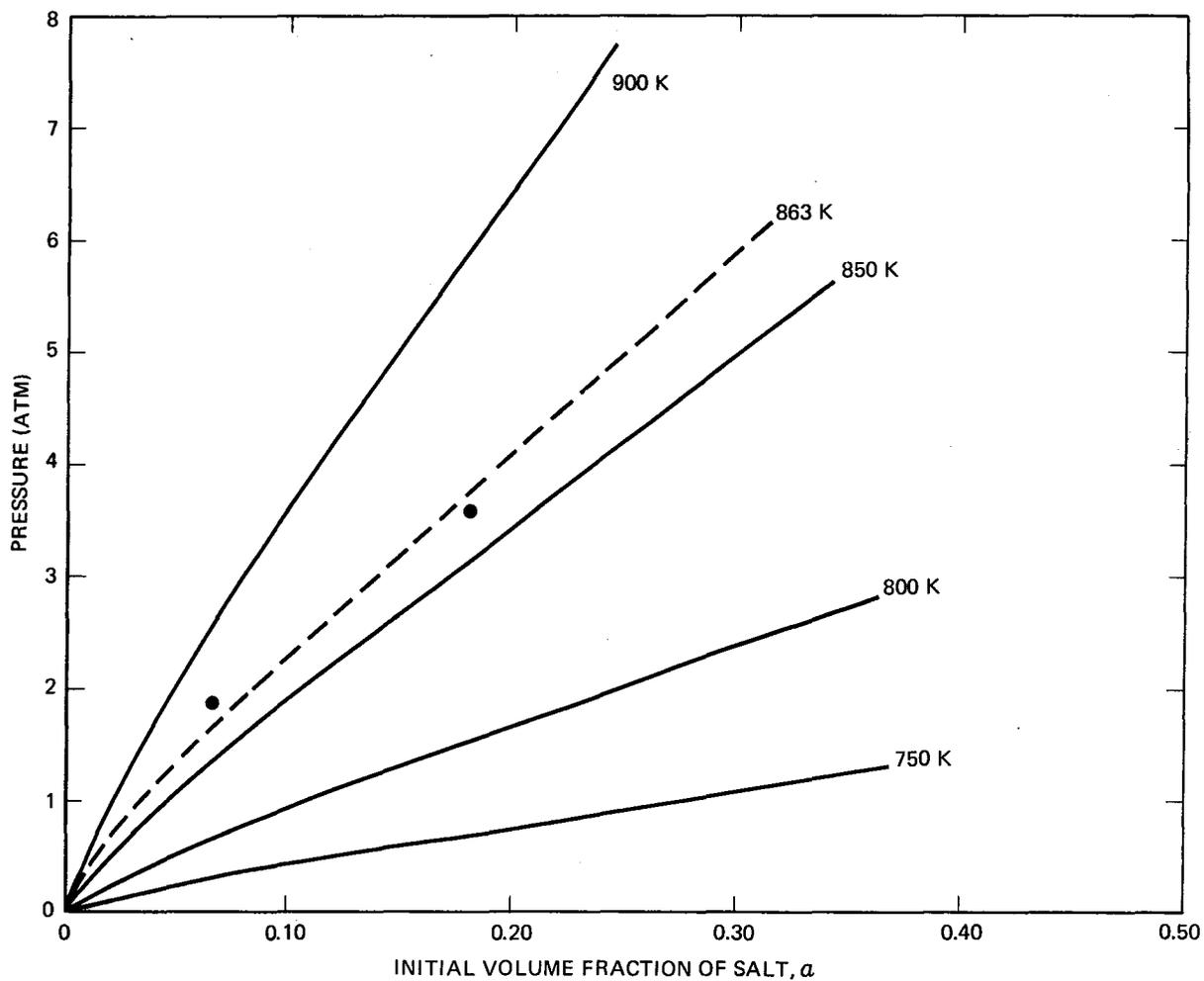


Figure 4. Pressure- α Isotherms for 60% NaNO_3 -40% KNO_3 (by Weight) Heated in a Sealed System. Two Experimental Data Gathered at 863 K Are Shown, Along With the Calculated 863 K Isotherm.

represents the behavior of a system open to the air. The effect of an inert cover gas is to reduce the oxygen partial pressure; the exact level of course depends upon design features and operational parameters such as cover gas purity, flow rate, and system tightness. The curves for 0.01 and 0.001 atm are reasonable representations of open systems with control by inert atmosphere flooding.

From Figure 5 it is evident that as temperature increases, the nitrite concentration rises. A temperature change of 100 K can cause as much as an order of magnitude change in the nitrite to nitrate ratio. It is also clear from Figure 5 that increasing the partial pressure of oxygen suppresses nitrite formation, in accordance with the Le Chatlier principle applied to Eq. (1). Decreasing the oxygen partial pressure by an order of magnitude causes approximately a factor of two increase in the nitrite-to-nitrate ratio.

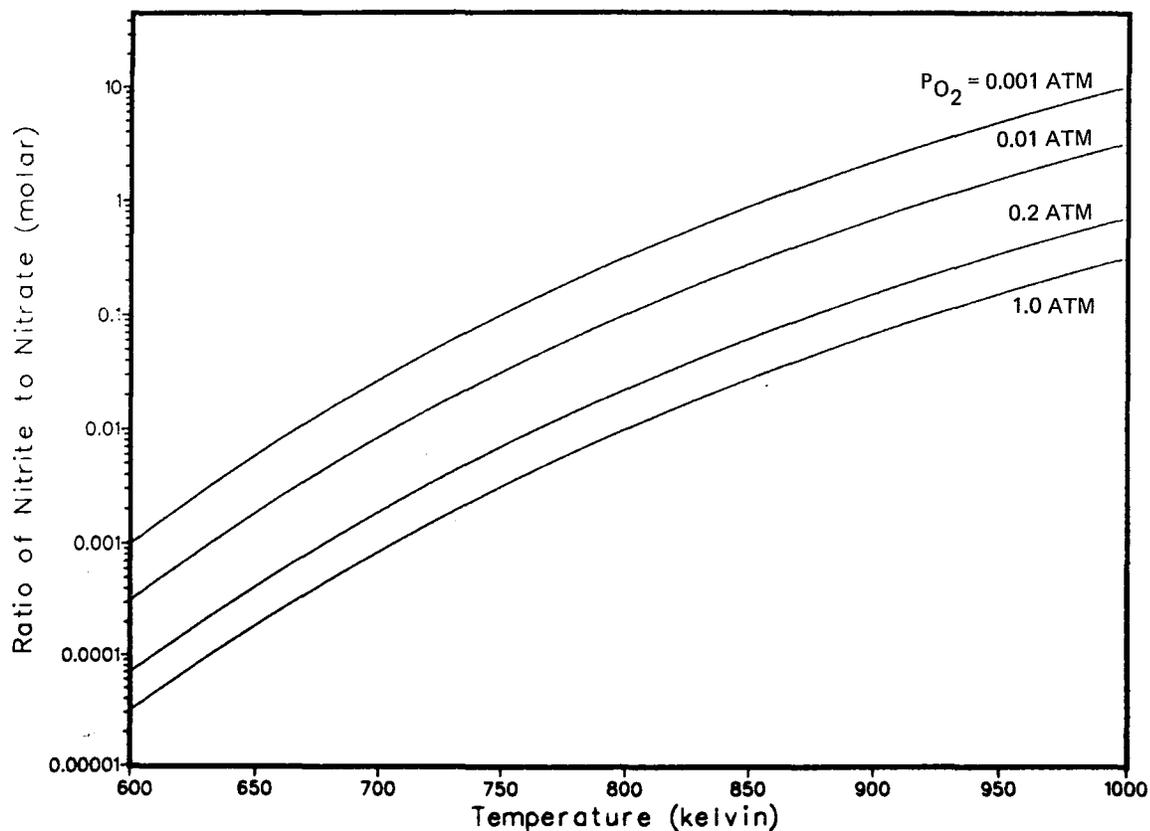


Figure 5. Composition-Temperature Relationships for 60% NaNO₃-40% KNO₃ (by Weight) Heated in an Open System Held at Various Constant Oxygen Pressures.

Summary

Pressure-temperature-composition relationships for heated drawsalt of the Partherm 430 composition (60% NaNO_3 -40% KNO_3 by weight) have been calculated for two system designs, a fixed-volume (sealed) system and a fixed-pressure (breathing or inert cover gas) system. In the analysis the following assumptions were made: 1) the only reaction of importance is nitrate-nitrite-oxygen equilibrium, 2) the liquid solution behaves ideally, and 3) equilibrium conditions obtain. For the sealed system, pressure-temperature and composition-temperature curves were generated for various initial salt volume fractions ranging from $\alpha = 0.1$ to 0.7 (see Figures 1 and 2). The validity of the assumptions and calculations was verified by comparing the pressures obtained in two experiments (conducted at 863 K and with initial salt volume fill fractions of 0.06 and 0.17) with calculated values.

For open (constant oxygen pressure) systems, composition-temperature curves (see Figure 5) were generated for various oxygen partial pressures. Increasing temperature and decreasing pressure cause increasing nitrate levels in the salt.

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