

THE PHASE DIAGRAM OF NaNO_3 — KNO_3 *

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ABSTRACT

The binary phase diagram of NaNO_3 and KNO_3 was studied using differential scanning calorimetry (DSC). The data more precisely defined the solidus and liquidus of an earlier phase diagram for this system. This phase diagram was modelled using regular solution theory. By fitting the model to the experimental data the regular solution parameters and the heat of mixing for the solid solution of NaNO_3 and KNO_3 were estimated.

INTRODUCTION

Interest in sodium and potassium nitrate chemistry has been heightened in recent years because of the potential application to energy systems. For example, molten sodium and potassium nitrate mixtures have been proposed for use in solar large power plants, both as storage media and as the high-temperature heat transfer [1,2]. These salts and their mixtures have low melting points (<520 K) or low-temperature eutectics and are relatively non-corrosive, chemically stable, and inexpensive, all desirable characteristics for industrial fluids.

The NaNO_3 — KNO_3 diagram, studied before by Bergman and Berul [3] and Kofler [4] and reviewed by Voskresenskaya [5], is reported to be an isomorphous binary with a minimum melting point (see Fig. 1). In the most recent study Kofler used a hot-stage-microscope technique to determine the solidus and liquidus. Bergman and Berul, using polythermal-visual techniques, determined a liquidus that differed slightly (≤ 10 K) from that of ref. 4.

Recently, an increasing number of calculations have been performed to predict complex phase diagrams [6,7]. Such calculations can often substitute for tedious and difficult experiments, and provide insight into the thermodynamic properties of these materials. We have completed our own experimental and theoretical investigation of the NaNO_3 — KNO_3 phase diagram and report the results here. To predict the liquidus and solidus in the NaNO_3 — KNO_3 system we wrote a computer code based on a fundamental treatment of the thermodynamics of solutions. By comparing the calculated phase diagram with experimental data, obtained by different scanning calori-

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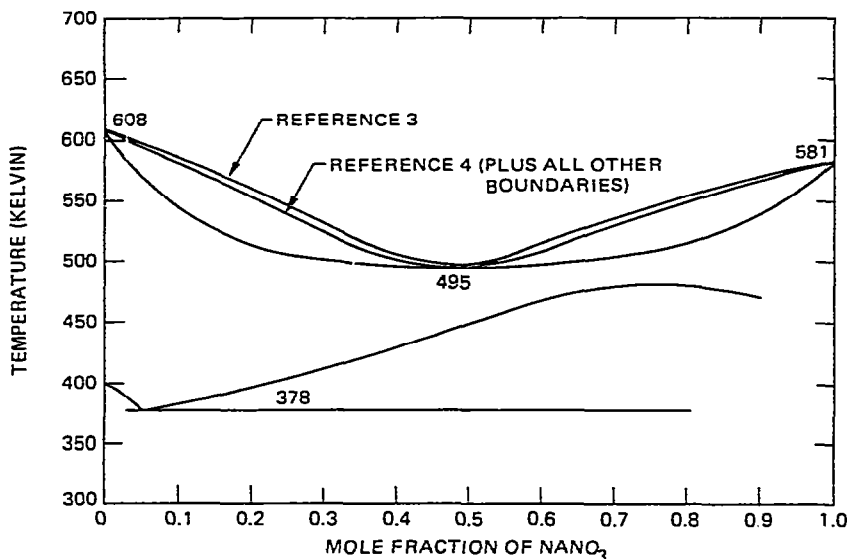


Fig. 1. Published phase diagrams of the NaNO₃-KNO₃ system.

metry, we gained insight into the behavior of nitrate salt solutions.

The remainder of this report is organized as follows: after briefly describing our experimental setup, we discuss the experimental results; the thermodynamic theory is then presented, following which the calculational results are compared with experiment.

EXPERIMENTAL TECHNIQUE

A Perkin-Elmer differential scanning calorimeter (DSC-2) was used for all measurements. The DSC was calibrated with In and K₂CrO₄ (Perkin-Elmer standards), whose temperatures of fusion and solid-state transition, respectively, are well known. The salt samples were heated several times at constant heating rates and the thermal spectra of their melting behavior were recorded.

All our samples consisted of reagent-grade sodium nitrate and potassium nitrate, dried at 380 K under vacuum for at least 12 h. Batches were prepared at 10 mole % intervals and ground in a micromill to assure uniformity. For certain composition ranges to be studied in more detail, additional batches were prepared at 2 mole % intervals. Small samples (<20 mg) were encapsulated in high-pressure stainless steel holders or hermetically sealed in aluminum pans.

EXPERIMENTAL RESULTS

A wide variety of DSC peak shapes were observed for the different NaNO₃-KNO₃ mixtures as illustrated in Fig. 2. In many of the broad peaks,

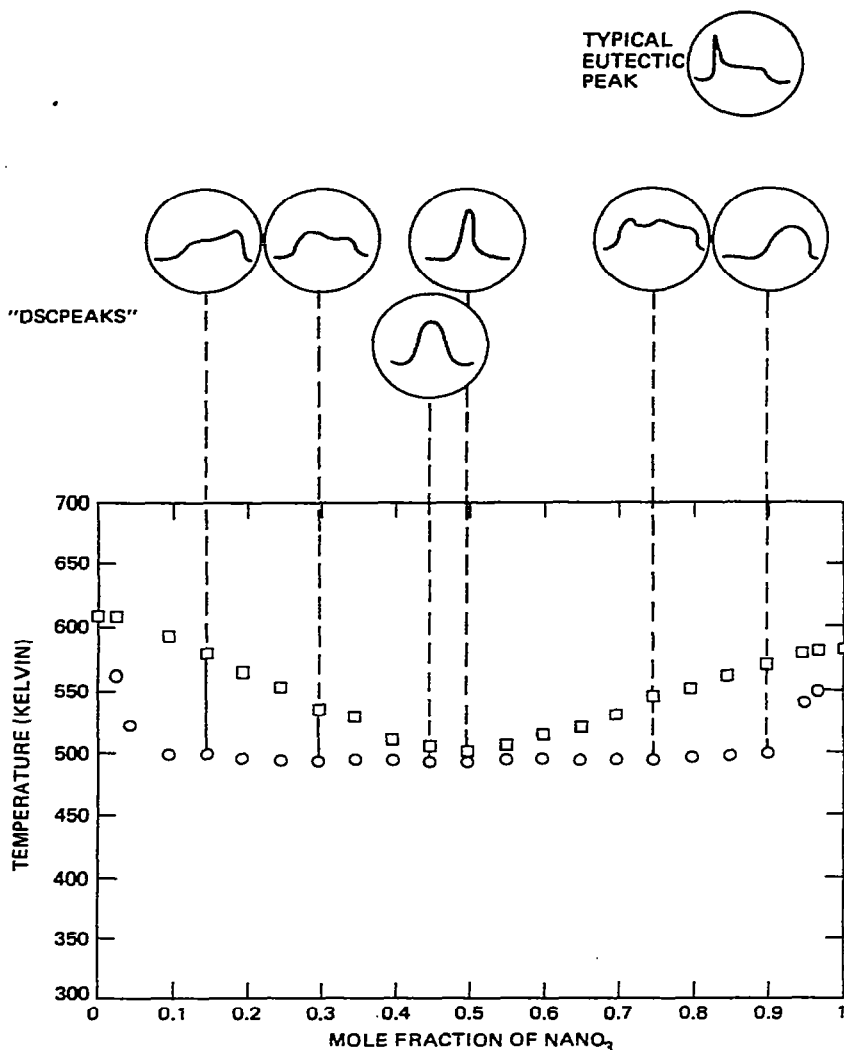


Fig. 2. DSC peaks for different NaNO_3 - KNO_3 compositions shown with the solidus and liquidus data.

local maxima are observed. Because the peaks are not sharp and some had gradually changing slopes, we had to determine the most reliable method for reporting the liquidus and solidus determined from the numerous peak shapes. The shape of DSC peaks depends upon the purity and composition, thermal contact of the sample in the pan, sample pretreatment, the DSC operating parameters, and the thermal transition being studied [8]. We made many DSC profiles of the salt mixtures using different heating rates (1.25 – 20 K min^{-1}), sample sizes (1 – 25 mg), sample pretreatment (prior grinding or fusion), and DSC energy scales (0.5 – 5 mcal sec^{-1}) to find consistent results for the liquidus and solidus. We found that using highly sensitive energy scales and heating rates of 10 K min^{-1} or less produced results that could be easily duplicated.

The lowest and highest temperatures at which the DSC traces (of melting the salt samples) deviated from a straight base line were consistent from run

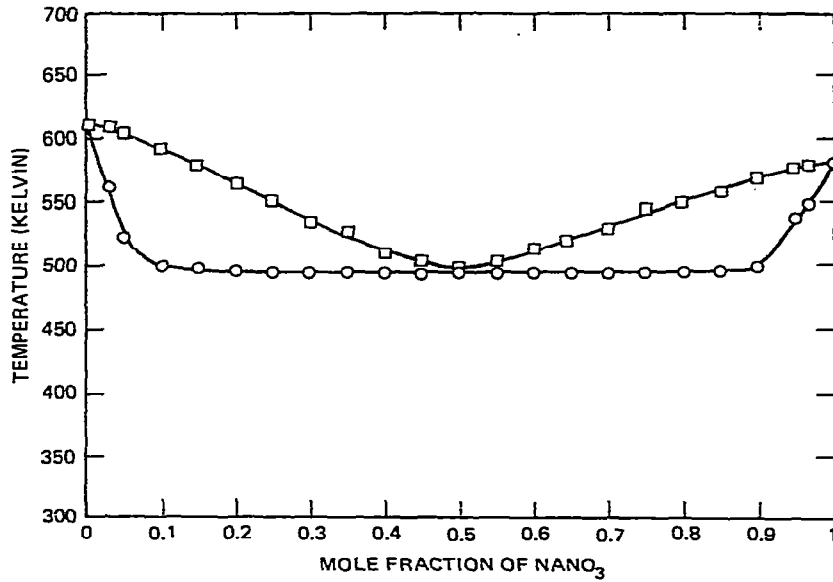


Fig. 3. Experimental DSC data for $\text{NaNO}_3\text{--KNO}_3$.

TABLE 1

DSC data for the $\text{NaNO}_3\text{--KNO}_3$ system

Mole fraction NaNO_3	Solidus temp. (K)	Liquidus temp. (K)
0.0	608	608
0.03	562	608
0.05	522	605
0.10	500	592
0.15	499	578
0.20	495	564
0.25	495	552
0.30	494	535
0.35	495	528
0.40	494	510
0.45	493	505
0.50	494	500
0.55	494	505
0.60	494	514
0.65	494	520
0.70	494	529
0.75	494	545
0.80	495	550
0.85	497	558
0.90	499	568
0.95	539	577
0.97	549	580
1.00	580	580

to run and sample to sample. Therefore, the initial and final points of deviation from the base line were chosen as the solidus and liquidus temperatures for the samples. These are plotted as a phase diagram in Fig. 3 and tabulated in Table 1. The discrepancy between samples was 3–4 K.

The experimentally determined solidus is much flatter than was previously reported. Although other systems, such as NaCl–KCl [9] or PbS–PbTe [10], have remarkably flat solidus boundaries between solid and liquid solutions, a horizontal solidus may indicate a eutectic with limited solid solution. To investigate this possibility we prepared samples which are known to form a eutectic with limited solid solution of KNO_3 (e.g., CsNO_3 and KNO_3 [11]), determined their DSC peaks, and compared these with the NaNO_3 – KNO_3 results. The DSC peaks observed in the vicinity of the eutectic were not the same shape as those observed for the NaNO_3 – KNO_3 . Rather, the DSC traces had the more classic peak shape described in ref. 12 and sketched in Fig. 2 for eutectic systems. One can visualize the situation where the solidus is nearly horizontal by studying Fig. 4, which schematically represents the free energy as a function of composition at the minimum melting temperature.

The flat solidus also led us to suspect that there may have been some contamination of the samples, such as due to water. To check this possibility

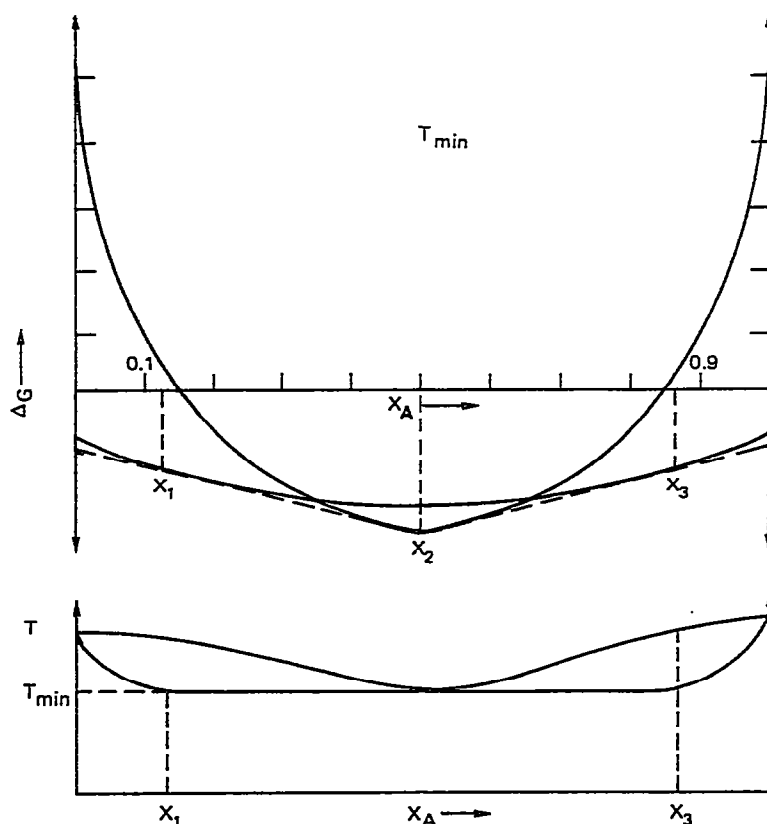


Fig. 4. A relationship between the free energy curves of solid and liquid solutions that could cause a very flat solidus in a binary solution.

we exposed several samples to high humidity. These samples had lower liquidus temperatures than did carefully dried samples, a fact which agrees with the trends in the $\text{KNO}_3\text{--NaNO}_3\text{--H}_2\text{O}$ ternary reported by Bergman and Shulyak [17]. We also checked our DSC samples for contamination from reaction with the air or decomposition. An IR spectrum was made of a DSC sample that had been repetitively cycled to high temperature. No decomposition or reaction with air or water was observed. Inspection of used pans showed no evidence of a reaction between the salts and pans.

Phase transformations of pure NaNO_3 and KNO_3 have been studied in great detail [13–16] and are reviewed in ref. 13. At 548.5 K sodium nitrate transforms from an ordered rhombohedral phase to a disordered rhombohedral structure. Potassium nitrate is orthorhombic at room temperature but undergoes a phase transformation at 403 K to a rhombohedral structure to become isostructural with NaNO_3 . On cooling, however, KNO_3 usually reverts to the orthorhombic phase via an intermediate and slightly less symmetric rhombohedral phase that exists from 383 to 397 K. Rao et al. [13] regard this form as metastable at the temperatures and pressures studied here, but they suggest it may appear in DSC experiments. Indeed, we did observe small DSC peaks at ~ 385 K or ~ 400 K in KNO_3 containing mixtures. The temperature was dependent upon composition and pretreatment of the samples.

Investigating the minimum temperature phenomenon further, we analyzed several DSC samples by powder X-ray diffraction to seek evidence of solid solution formation of $\text{NaNO}_3\text{--KNO}_3$, such as is found in the pure substances. However, although we quenched NaNO_3 and KNO_3 mixtures from above and below the liquidus, two distinct and sharp crystal patterns were always obtained for rhombohedral NaNO_3 and orthorhombic KNO_3 by X-ray diffraction. No homogeneous patterns for a $\text{NaNO}_3\text{--KNO}_3$ solid rhombohedral solution were observed. Rhombohedral KNO_3 could not be quenched into the samples. We feel that a technique such as high-temperature X-ray diffraction is necessary to observe the solid solution.

THEORY

The behavior of binary systems of molten salts having a common anion has received considerable theoretical attention [18–21]. Examining his measurements of heat of mixing of liquid NaNO_3 and KNO_3 , Kleppa [21] found that regular solution theory applies. Measurements of the surface tension [22] of 50/50 (Na/K) NO_3 agree well with calculations using the measured heat of mixing and substantiate the applicability of regular solution theory to this system of salts.

A regular solution is a mixture that deviates from ideal solution behavior in a simple manner. The entropy of several components mixed to form a regular solution is purely configurational, as with ideal solutions

$$\Delta S_{\text{mix}} = X_A \ln X_A + X_B \ln X_B \quad (1)$$

Regular solutions have a non-zero enthalpy of mixing, and an often-used

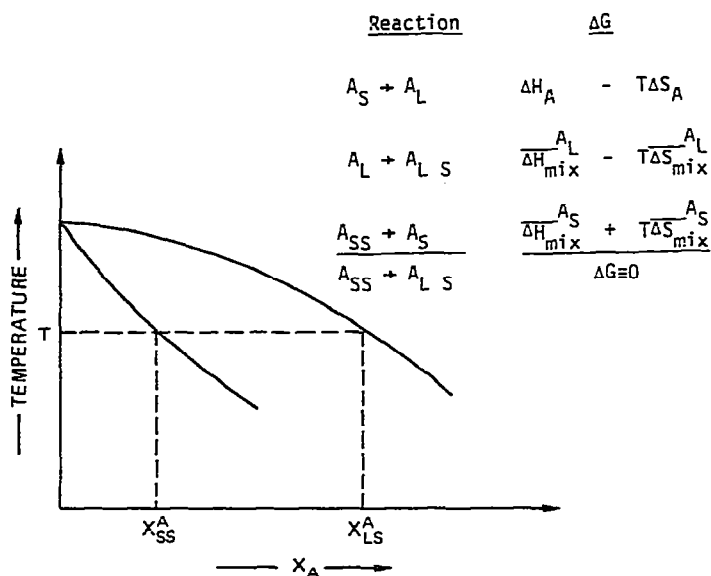


Fig. 5. Section of a general binary phase diagram. A solid solution X_{SS}^A is in equilibrium with a liquid solution X_{LS}^A at temperature T ; therefore, the free energy of the reaction is 0. For $A_S \rightarrow A_L$, ΔH_A and ΔS_A refer to the melting of component A. For $A_L \rightarrow A_{LS}$ and $A_{SS} \rightarrow A_S$, ΔH and ΔS refer to the partial molar quantities for mixing A.

form is

$$\Delta H_{mix} = X_A X_B (a + bX_A + cX_A X_B) \quad (2)$$

where X_A is the mole fraction of the component having the smaller size ($A = \text{NaNO}_3$ in this case) and a , b , and c are empirical constants. As derived from calorimetric studies [21] of liquid solutions of NaNO_3 and KNO_3 (618–723 K) the values of a , b , and c are -408 , -68 , and ~ 0 . cal mole $^{-1}$.

One can express the thermodynamic equilibrium of a solid solution and a liquid solution of A and B as sketched in Fig. 5. The overall free energy of the reaction $A_{SS} = A_{LS}$ must be zero because the solid and liquid solutions are at equilibrium. From Fig. 5 we see that the free energy of the overall reaction for component A ($A_{SS} = A_{LS}$) may be expressed as

$$\Delta G \equiv 0 = (\Delta H_A - T \Delta S_A) + (\overline{\Delta H}_{mix}^{A_L} - T \overline{\Delta S}_{mix}^{A_L}) - (\overline{\Delta H}_{mix}^{A_S} - T \overline{\Delta S}_{mix}^{A_S}) \quad (3)$$

(i) (ii) (iii)

The expressions ΔH_A and ΔS_A are the enthalpy and entropy of melting component A. The partial enthalpies and entropies of mixing in either the solid or the liquid solution are given by $\overline{\Delta H}_{mix}^A$ and $\overline{\Delta S}_{mix}^A$.

Equation (3) can be evaluated when assumptions and substitutions are made. Expression (i) is simply the free energy of fusion of component A at some temperature other than the melting point (where it is zero). The terms in (i) are corrected for temperature variations by

$$\Delta H_A = \Delta H^0 - \int_T^{T^{MP}} (C_{pL} - C_{pS}) dT \quad (4)$$

$$\Delta S_A = \Delta S^0 - \int_T^{T_{MP}} \frac{(C_{pL} - C_{pS})}{T} dT \quad (5)$$

where T_{MP} is the melting point of component A, and ΔH_A^0 and ΔS_A^0 are the enthalpy and entropy of fusion of A at its melting point. The correction terms arise from the difference in heat capacities between the solid (C_{pS}) and the liquid (C_{pL}) [23].

In order to evaluate (ii) and (iii), both the solid and liquid solutions are assumed to exhibit regular solution behavior. The partial molar enthalpy of mixing for component A, $\overline{\Delta H_{mix}^{AS}}$ or $\overline{\Delta H_{mix}^{AL}}$ (in the solid or liquid solution, respectively), may then be found by applying to eqn. (2) the Gibbs–Duhem equation

$$\overline{\Delta H_{mix}^A} = \Delta H_{mix} - X_B \frac{d \Delta H_{mix}}{dx_B} \quad (6)$$

The value of $\overline{\Delta H_{mix}^{AL}}$ can be found explicitly from Kleppa's values [21]. A similar equation can be written for the equilibrium of component B in both the solid and liquid solutions. The differences between the equations for components A and B are introduced by the asymmetry factor b in the enthalpies of mixing and are carried through the Gibbs–Duhem equation to obtain $\overline{\Delta H_{mix}^A}$ and $\overline{\Delta H_{mix}^B}$, the partial molar enthalpies of mixing.

Substituting eqns. (1), (2), and (4)–(6) into (3) results in two non-linear equations in T and X_A or X_B . A computer routine was written to simultaneously solve the two forms of (3) for NaNO_3 and KNO_3 . The routine incorporated a library algorithm based on an iterative variation of Newton's method and Gaussian elimination in a manner similar to the Gauss–Seidel process [24]. The program was supplied with the values from ref. 21 for a and b in the enthalpy of mixing of liquid solutions (c was assumed to be zero) and the appropriate values from ref. 25 of C_{pL} , C_{pS} , ΔH^0 and ΔS^0 for NaNO_3 and KNO_3 . The value of a for the solid solution was systematically increased until the minimum melting point that was calculated coincided with the experimentally determined minimum melting point. For NaNO_3 – KNO_3 solid solutions the value of $a = +1500 \text{ cal mole}^{-1}$ gave the correct minimum melting point. Changing a from $1400 \text{ cal mole}^{-1}$ to $1500 \text{ cal mole}^{-1}$ lowered the minimum melting point from 500 K to 495 K . The value of b was then varied to try to improve the fit of the model to the experimental data. If b is decreased from 0 to $-500 \text{ cal mole}^{-1}$, the minimum melting point location is shifted from 495 K at $X_{\text{NaNO}_3} = 0.483$ to 501 K at $X_{\text{NaNO}_3} = 0.453$. Because b is primarily an asymmetry factor (and the phase diagram was experimentally observed to be symmetric) the best fit was for $b = 0 \text{ cal mole}^{-1}$.

CALCULATIONAL RESULTS AND COMPARISON WITH EXPERIMENT

Osculating phase boundaries are predicted for the equilibrium of solid and liquid solutions [26], and were generated by the calculational routines.

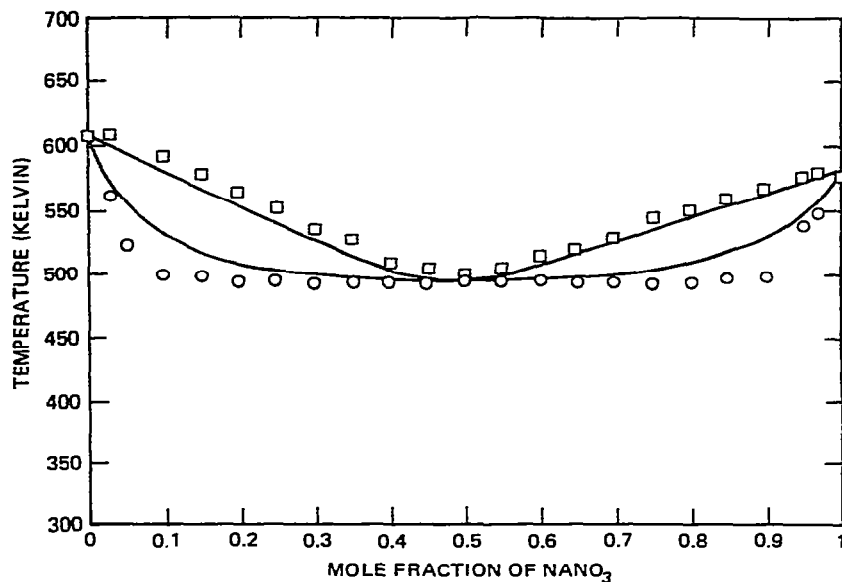


Fig. 6. Experimental data points and the calculated liquidus and solidus.

Figure 6 compares our data with the results of the computer program for $a = +1500 \text{ cal mole}^{-1}$ and $b = 0 \text{ cal mole}^{-1}$ for solid solutions of NaNO_3 — KNO_3 . The expression for the enthalpy of mixing of the solid solutions is given by eqn. (7).

$$\Delta H_{\text{mix}}^{\text{ss}} = X_{\text{NaNO}_3} X_{\text{KNO}_3} (1500) \text{ cal mole}^{-1} \quad (7)$$

The positive value of a for the solid solutions indicates a tendency towards clustering of like ions in the solid solutions.

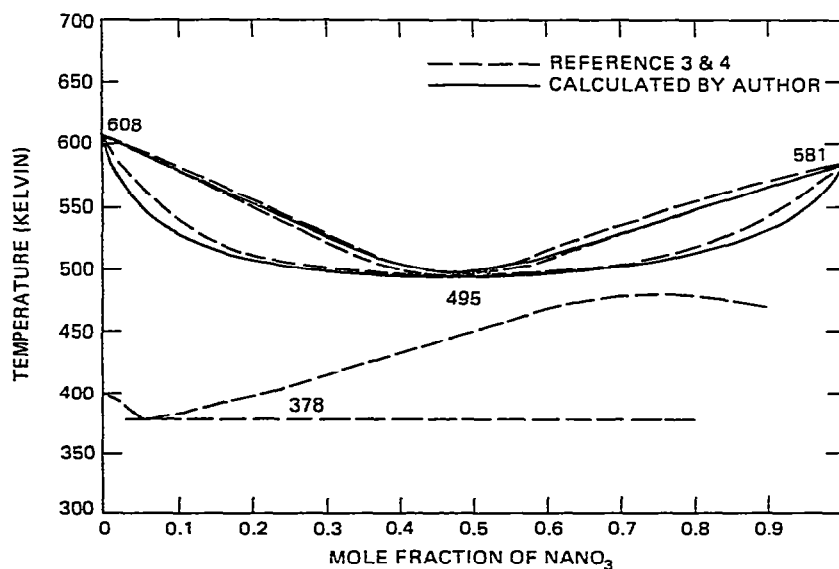


Fig. 7. Comparison of the calculated and published NaNO_3 — KNO_3 phase diagrams.

The calculated phase diagram is overlaid on the published phase diagrams in Fig. 7. The liquidus determined in this work, the previously reported liquidus, and the liquidus from our model are in good agreement across the phase diagram. The solidus we determined experimentally is lower than that from our model or previously determined solidus. The discrepancies are as large as 30 K between the previously determined solidus and the present work for the 0.1 and 0.9 mole fraction mixtures of NaNO_3 with KNO_3 . We could not resolve this disagreement in the present and prior data. The experimentally determined solidus lies closer to the calculated phase diagram than to the published phase diagram. The calculated solidus is lower than the previously determined experimental solidus.

In our attempt to analytically describe the thermodynamics of NaNO_3 — KNO_3 mixtures, several assumptions and approximations were made. The mixing parameters, a and b , may be slightly temperature dependent, but this was neglected. Kleppa [21] made his measurements of the enthalpy of mixing at higher temperatures (618–723 K) than the temperatures studied here (490–610 K).

For systems that deviate from randomness, alternative expressions have been defined [23] for the free energy of mixing, such as

$$\Delta G_{\text{mix}} = X_A X_B \left(1 - \frac{X_A X_B K}{ZRT} \right) - T \Delta S_{\text{mix}} \quad (8)$$

Here, K is a constant, Z is the coordination number, and R and T have their usual meanings. The value of Z was estimated to be 5 based on ref. 27. This form for the free energy of mixing was incorporated into the computer program to calculate the phase diagram, and a number of values of K ranging from 0 to 2000 cal mole⁻¹ were tried. The results were similar to the regular solution treatment and the solidus was not flatter. Although a more elaborate description of the excess entropy contributions — such as using Legendre polynomials [6] — may contribute to the accuracy in describing the $\text{NaNO}_3/\text{KNO}_3$ thermodynamics, we did not explore that possibility.

NaCl—KCl CALCULATIONS

As verification of the validity of the computer program, it was applied to NaCl—KCl, a system homologous to NaNO_3 — KNO_3 . The mixing parameters for liquid solutions have been determined to be $a_L = -490$ cal mole⁻¹ and $b_L = -65$ cal mole⁻¹ [18]. Tobolsky [28] calculated the enthalpy of mixing for a solid solution of 50/50 NaCl/KCl to be 1188 cal mole⁻¹. We assumed that the solid solutions would exhibit regular solution behavior and that the asymmetry factor b was zero for the solid solutions of NaCl—KCl. Therefore, using eqn. (2), a_S is 4(1188) cal mole⁻¹ or 4752 cal mole⁻¹. This value of a_S and the above values of a_L and b_L were used in calculations of the NaCl—KCl phase diagram (see Fig. 8). The resulting liquidus and solidus had a minimum melting point of 880 K, which is within about 4% of a recent experimental determination [9] (918 K). The experimental minimum melting point can be obtained exactly by changing the value of a_S to 3200

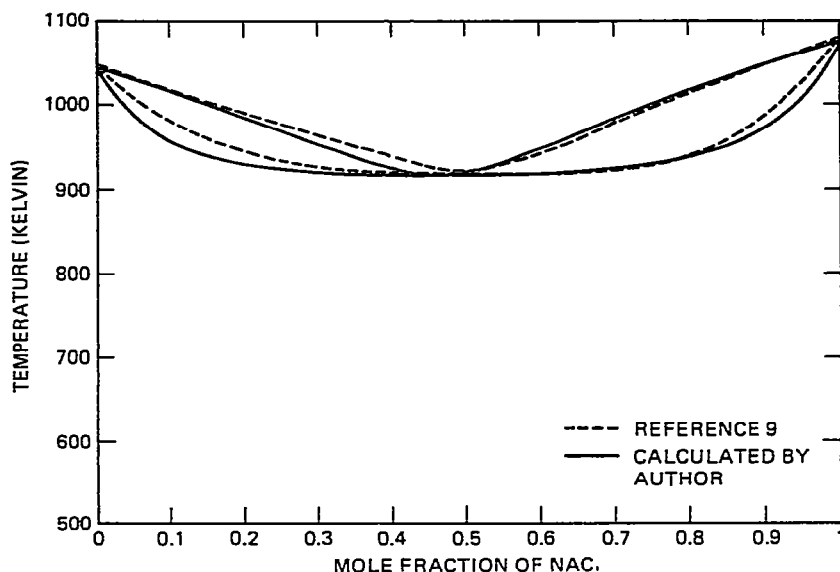


Fig. 8. Comparisons of the calculated and published NaCl—KCl phase diagrams.

cal mole⁻¹. The corresponding heat of mixing of solid 50/50 (Na/K)Cl is then 800 cal mole⁻¹. Tobolsky pointed out that the value of his heat of mixing of solid NaCl/KCl was approximate; therefore, a value of 800 cal mole⁻¹ may be considered very reasonable.

CONCLUSIONS

The phase diagram of NaNO₃—KNO₃ was studied using differential scanning calorimetry. The solidus was determined to be flatter than previously reported. A computer code was developed from regular solution theory and thermodynamics that approximated the experimental data. Using the code we estimated the heat of mixing of the solid solution to be 375 cal mole⁻¹ for an equimolar mixture of NaNO₃ and KNO₃. The computer code was also successfully applied to the NaCl—KCl phase diagram. In contrast to the previously reported value of 1188 cal mole⁻¹, the heat of mixing of 50/50 (Na/K)Cl was calculated to be 800 cal mole⁻¹. For future work on more complex systems, the results of this study can serve as a suitable starting point.

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