Polymorphism in the KCl–KF and KCl–NaCl Systems at Elevated Pressures and Temperatures*

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The pressure-induced polymorphic transition in the salt systems KCl–KF and KCl–NaCl was investigated by dilatometry from 25°C to 900°C and at pressures to 50 kb. The transition in these binary systems is similar to the $Fm3m \rightleftarrows Pm3m$ phase change in KCl. KF does not measurably affect the transition pressure of KCl at any temperature up to 900°. The effect of NaCl upon KCl is also small below 300°. This is understandable because of the low solubility of KF and NaCl (below 300°) in KCl. The transition pressure, (P_{tr}), its width (P_w), and the transition volume (ΔV_{tr}) indicate that the transition observed in the KCl–KF system, and in the KCl–NaCl system at temperatures below 350°, occurs in the KCl-rich phase. However, at temperatures above 350°, NaCl raises P_{tr}, broadens P_w, and decreases ΔV_{tr}. At 800° the elevation in P_{tr} is approximately proportional to mole fraction (X) NaCl. For a given composition, ΔV_{tr} also decreases as T increases. At high T and high X NaCl, $\Delta V_{tr} \rightarrow 0$. The 400°, 500°, 600°, 700°, and 800° isotherms for the P_{tr} vs X NaCl curves were extrapolated to X NaCl = 1. This procedure yields hypothetical P_{tr} vs T and ΔV_{tr} vs T curves for this polymorphic transition in pure NaCl. This extrapolation indicates that for pure NaCl $\Delta V_{tr} = 0$ at 300°; $\Delta V_{tr} > 0$ when $T < 300°$. At 300° the extrapolated value of P_{tr} is 14 kb. These curves aid in understanding the conflicting reports for a polymorphic transition in pure NaCl in the pressure range of 12–30 kb.

I. INTRODUCTION

It is well known that the alkali halides occur in two crystal modifications: the "rock salt" form, space group $Fm3m$, and the CsCl form, space group $Pm3m$. Polymorphism between these two structure types is known to take place in over half of these compounds.[1]

This group of salts offers a good opportunity for examination of atomic or periodic trends in properties of ionic compounds, particularly of the phase transition between these two relatively simple cubic modifications, $Fm3m$ and $Pm3m$. Indeed, a regular variation in the fusion properties of the $Fm3m$ form of these salts with interatomic spacing (or mean distance of closest approach of ions in the solid phase) is known (7).

[1] The literature on the phase transitions in this class of compounds is extensive. For further information the reader is referred to papers by Tosi and Fumi (*1*), Schumacher (*2*), Tosi (*3*), Klement and Jayaraman (*4*), and Darnell and McCollum (*5, 6*).

In a previous paper Darnell and McCollum (5) have examined the polymorphic transition in the potassium and rubidium halides from room temperature to temperatures near the triple point, $Fm3m \rightleftarrows$ liquid $\rightleftarrows Pm3m$. In a subsequent paper these authors have made a similar study of the polymorphic transition in the binary solid solutions of the system KCl–KBr and KCl–RbCl (6). The first of these salt systems illustrates the effects of anionic substitution (Br^- for Cl^-), the latter cationic substitution (Rb^+ for K^+), upon this polymorphic transition. This paper is a continuation of the study of the effects of ionic substitution upon this polymorphic transition. Here we examine the effects of ionic substitution upon the $Fm3m \rightleftarrows Pm3m$ transition in KCl through study of the systems KCl–KF and KCl–NaCl.

II. EXPERIMENTAL

A. *Materials*

The salts KCl, NaCl, and KF used in this work were Mallinckrodt analytical reagent grade. The procedures used for drying these salts and the preparation of their solid solutions or mixtures are described elsewhere (5, 6). In the binary systems studied in an earlier work (6) the salts RbCl and KBr formed continuous solid solutions with KCl, even at room temperature. NaCl, however, is completely miscible with KCl only at temperatures above 500° (8, 9, 10, 11). X-Ray diffraction measurements made at ambient temperature and pressure of samples prepared for these phase transition studies show essentially pure phases of the component salts. These diffraction measurements were made upon samples which had been heated at 250° for several hours. Metastable solid solutions of KCl and NaCl can be obtained, however, at room temperature by a quench process (11). In the KCl–KF system, KF is only very slightly soluble in KCl at room temperatures (12); its solubility in KCl at high temperatures is not known. Samples of KCl–KF and KCl–NaCl were heated at 250° for at least an hour within the high-pressure apparatus (at a pressure of ~ 2 kb) before carrying out the phase transition studies upon them.

B. *Apparatus and Procedure*

These phase transition studies were carried out utilizing a piston–cylinder apparatus. The salt sample or pellet was heated by a graphite furnace within the high-pressure chamber. A piston displacement method was used for detection of the polymorphic change and the measurement of the transition volume. This apparatus and technique are similar to those employed by Darnell and McCollum in their study of the polymorphic transition in KCl, RbCl, KBr, KCl–RbCl, and KCl–KBr (5, 6). Sample temperatures were determined from a thermocouple placed within the salt sample in the high-pressure chamber (5). No correction has been made for the effect of pressure upon the thermocouple emf. This pressure effect is, however, small (i.e., less than 1 %) for chromel–alumel junctions at pressures below 25 kb.

III. RESULTS

A. *KCl–KF*

Mixtures with the compositions 90 mole % (m/o) KCl and 75 m/o KCl were examined at approximately 100° intervals from room temperature to 900° over the

pressure interval 5 to 45 kb. In all cases both samples showed a polymorphic transition at a pressure corresponding to P_{tr} found for pure KCl at the same corresponding temperature (5). Furthermore, the width of this transition pressure interval (P_w) (5, 6) in these mixtures was approximately the same as P_w measured for pure KCl (5). The transition volume (ΔV_{tr}) for these compositions was found to be approximately 90% and 75%, respectively, of ΔV_{tr} measured for pure KCl at the same corresponding temperature (5).

B. *KCl–NaCl*

Mixtures with compositions between 5 and 95 m/o KCl were examined. Data for the mean transition pressure (P_{tr}^m) (6) found for the polymorphic phase change in binary salts in this system at isotherms 300 through 800° are shown in Fig. 1. The
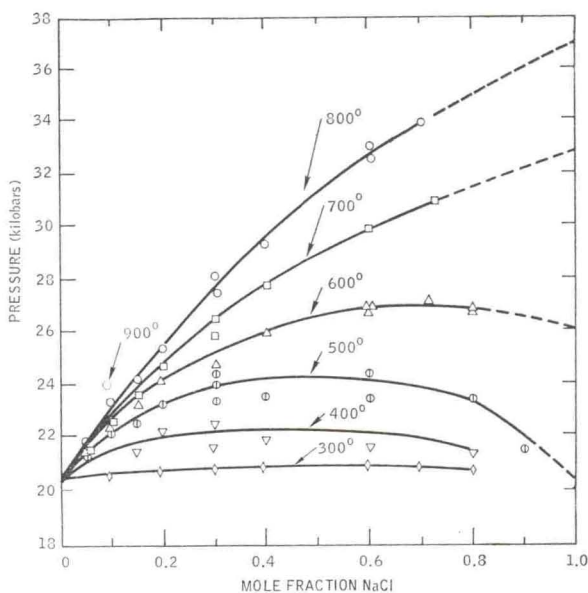

FIG. 1. Polymorphic transition pressure (P_{tr}^m) of salts in the KCl–NaCl system in the temperature range 300–900°.

width of the polymorphic transition pressure interval (P_w) measured for salts in this system is shown for two temperatures, 500 and 800°, in Fig. 2. The volume change which occurs during the polymorphic transition in these salts was also measured over the temperature interval 300° to 800° at 100° intervals. These transition volume data are shown in Fig. 3. Below 300° the transition of these mixtures is so sluggish and hysteresis so large that no reliable and reproducible extrapolation could be made from the pre- and post-transition *P–V* curves; thus no P_{tr} and ΔV_{tr} data are given for temperatures below 300°. From Fig. 3 it can be seen that the phase transition volume (ΔV_{tr}) becomes very small at high temperatures and at high mole fractions of NaCl. The highest composition of NaCl (95 m/o) for which a transition volume
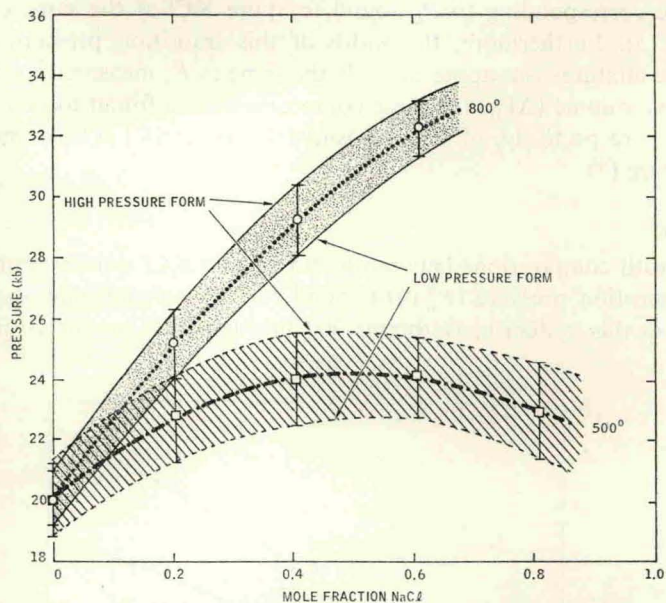
FIG. 2. Polymorphic transition pressure of salts in the KCl–NaCl system showing width of the transition pressure interval (P_w) at 500° and 800°.
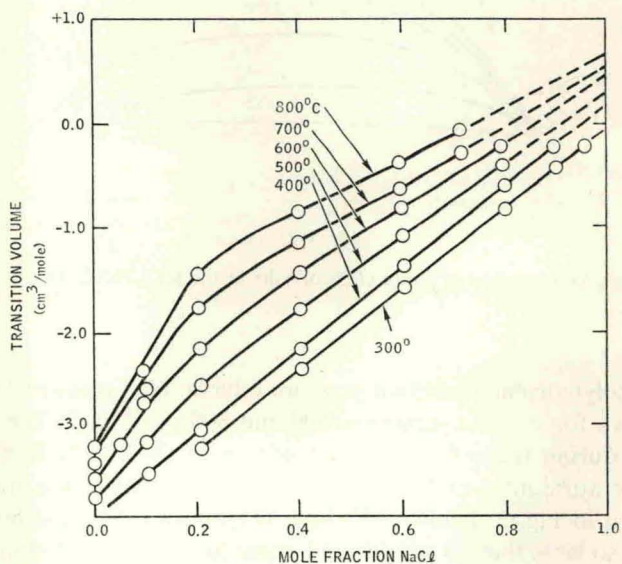

FIG. 3. Transition volume (ΔV_{tr}) of the pressure-induced phase change for salts in the KCl–NaCl system at the isotherms 300°–800°.

could be measured by this dilatometric method at a given temperature is shown in Fig. 3. The corresponding composition limit for which a transition pressure could be obtained at a given temperature is shown in Fig. 1.

IV. DISCUSSION

A. *KCl–KF*

The results from the phase transition studies on the KCl–KF system show that KF does not measurably affect the polymorphic transition in KCl at any temperature up to the melting-point curve for this system. The polymorphic transition observed in these mixtures is identical to the transition observed for pure KCl (5) at all temperatures up to 900°. Furthermore, the width of the transition pressure interval (P_w) (i.e., the two-phase region (6)) is not affected by the addition of KF. Most convincing, however, is that the transition volume measured for each of the binary mixtures is equal to the mole fraction KCl in the given mixture times the molar transition volume of pure KCl (5). No polymorphic transition was detected in these binary salts corresponding to a transition in the KF-rich phase. Piermarini and Weir (13) and Pistorius and Synman (14) have reported a transition in KF at pressures of 35 and 14.6 kb, respectively. Darnell and McCollum (5) detected no transition in KF at any pressure up to 45 kb and at any temperature up to 800°. Furthermore, Pistorius (15) found no break in the melting curve of KF at pressures up to 45 kb which suggests that KF has no solid–solid transition at pressures below 45 kb (at temperatures near the melting curve). The results from this work show that KF has no detectable effect on the polymorphic transition properties P_{tr}, P_w, and ΔV_{tr} of the KCl-rich phase. It would seem reasonable to assume this is due to the low solubility of KF in KCl in the solid phase (i.e., probably below 5 m/o) as indicated by the temperature–composition diagram for this system at atmospheric pressure (12).

B. *KCl–NaCl*

The results from the polymorphic transition studies carried out here on this system exhibit three types of solubility behavior. These results are, in general, interpretable in view of the temperature–composition diagram of the KCl–NaCl system at atmospheric pressure[2] (8, 9, 10, 11). Below 300° the mutual solid solubility is limited to less than 10 m/o, between 300 and 500° the solid solubility becomes appreciable, and above 500° these two salts become miscible in all proportions. The solid–solid miscibility curve is asymmetrical with its upper consolute point at 500° and at 70 m/o NaCl. The pure salts, KCl and NaCl, melt at 776° and 801°, respectively. The liquidus–solidus curve is symmetrical with a minimum at 650°. Thus for purposes of this discussion we will consider (a) the region of limited solid–solid solubility, $t < 300°$, (b) the region of extensive solid–solid solubility, 300–600°, and (c) the region of complete miscibility, $t > 600°$. In the first case (a) the polymorphic transition of salts in the KCl–NaCl system is similar to salts in the KCl–KF system. Below

[2] Pressure would be expected to decrease solid solubility in the KCl–NaCl system when the salts are in the *Fm3m* form since the volume increases upon the formation of the solid solution (11). Data are not available from which to estimate the effect of pressure on the solid solubility of these salts when in the *Pm3m* form.

pressures of 50 kb (the upper pressure limit of these studies) only a single polymorphic transition was observed. This transition pressure is essentially identical to the transition curve observed in pure KCl (5). In addition, the width of the transition pressure interval (P_w) is also the same as measured in pure KCl (5, 6). The volume change for this transition is proportional to the mole % KCl in the mixture and furthermore extrapolates to $\Delta V_{tr} = 0$ at m/o KCl = 0 (Fig. 3). Thus these results indicate that the transition observed here occurs in the KCl-rich phase. Thus no polymorphic transition, which could be attributable to a phase change in the NaCl-rich phase, was observed at pressures below 50 kb.

In the second type of behavior (b), the transition pressure of KCl is initially raised by the addition of NaCl. However, P_{tr}^m shows a plateau in the pressure–composition isotherm (40 m/o NaCl at 400°, 30 m/o NaCl at 500°, Fig. 1). The width of the pressure interval over which polymorphic transition occurs increases as compared to its width at 300° whereas in single-component systems this interval was found to decrease with increasing temperature (6). Nonlinearity in the ΔV_{tr} vs composition curve first appears at the 500° isotherm. The appearance of a plateau in P_{tr}^m vs composition at ~ 20 m/o NaCl on the 400° isotherm and at ~ 35 m/o NaCl on the 500° isotherm (Fig. 1) suggests the boundary of the solubility limit of NaCl in KCl at this elevated pressure of ~ 22 kb. Indeed this is a somewhat higher temperature than the boundary of the solid–solid solubility curve at atmospheric pressure (11). This is in agreement with our estimate for the effect of pressure on this solid–solid solubility of NaCl in KCl which was calculated by us from the ΔV and ΔS of formation of this solid solution (11).

In the third case, as illustrated by temperatures above 600°,[3] P_{tr}^m is shifted to higher pressures as the mole % NaCl is increased. This occurs up to 70 m/o NaCl at the 700 and 800° isotherms. The polymorphic transition volume has become so small at this composition and temperature (Fig. 3) that it is measured only with difficulty. At 800°, P_{tr}^m vs X (NaCl) is approaching linearity, similar to the case of KCl–RbCl studied previously (6). At 900° the polymorphic transition was measured at only one composition (10 m/o NaCl) due to the nearness of this transition to the melting curve of this binary system (8).

The width of the polymorphic transition pressure interval (P_w) decreases as the temperature is increased from 500° to 800° (see Fig. 2). This suggests that the solid solutions involved may be approaching more ideal behavior at this higher temperature. Part of this decrease in P_w is also probably due to less hysteresis at the higher temperature (5, 6). The polymorphic transition pressures measured here for the KCl–NaCl system are markedly different from the transition pressure of 110 kb reported for KCl (40 m/o)–NaCl (60 m/o) by Jamieson (16). However, Jamieson's studies were made at room temperature upon metastable samples (16) containing phases with at least three different compositions. It is pointed out that the results from measurements carried out in the present work were made upon annealed mixtures and thus represent results on phases which are in all likelihood near equilibrium solubility conditions. It appears that further work upon NaCl-rich solutions of the KCl–NaCl

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[3] The P_{tr}–composition isotherm at 600° shows some indication of a plateau at 60 m/o NaCl. It is probable that the solid–solid consolute point has been shifted from 500° and 60 m/o at 1 atm to this higher temperature at this higher pressure.

system, similar to Bassett's (*17*) phase studies using high-pressure X-ray diffraction upon pure NaCl, is needed.

We wish to point out the rather surprising implications which one might anticipate for the transition in pure NaCl based upon extrapolation of the P_{tr}^m vs X (NaCl) (Fig. 1) and ΔV_{tr} vs X (NaCl) (Fig. 3) to the composition of pure NaCl. Such extrapolated values of P_{tr}^m and ΔV_{tr} from several of the isotherms are shown in Fig. 4.
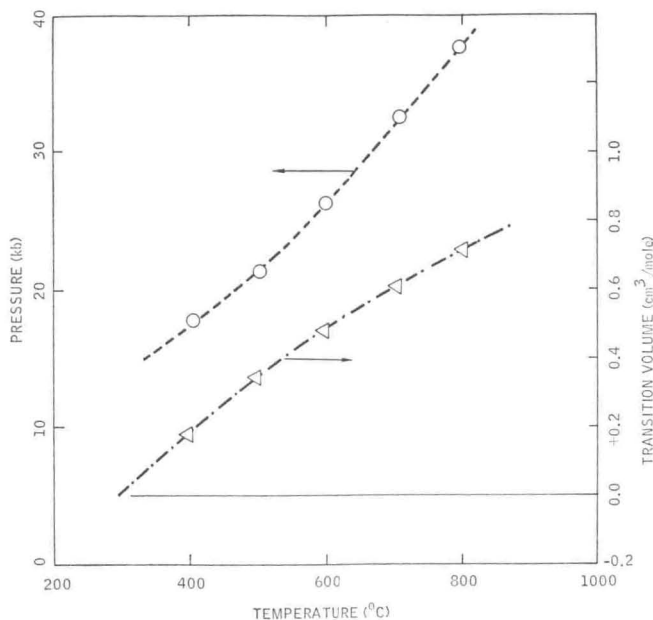

FIG. 4. Transition pressure (P_{tr}^m) and transition volume (ΔV_{tr}) obtained from extrapolation of the curves P_{tr}^m vs X (NaCl) and ΔV_{tr} vs X (NaCl) to X (NaCl) = 1 at the isotherms 400°–800°.

It is interesting to note that the extrapolated value for ΔV_{tr} is positive for this pressure-induced transition at temperature above 300°. Therefore this hypothetical curve for NaCl predicts, for thermodynamic reasons, that no polymorphic transition of this type is possible between 300° and 800°. These hypothetical curves suggest that some transition phenomena may be occurring in NaCl at temperatures below 300° in the pressure range of 15 kb which may be connected with the transitions reported by Evdokimova and Vereshchagin (*18*), Larson (*19*), and by Pistorius (*20*) for NaCl.

V. CONCLUSIONS

A. *KCl–KF*

It is not possible to examine the effect of anionic substitution of F$^-$ for Cl$^-$ upon the polymorphic transition in KCl because of the limited solid solubility of these two salts even at temperatures approaching the melting curve.

B. *KCl–NaCl*

At elevated temperatures ($> 600°$) where NaCl becomes completely miscible in KCl, the cationic substitution of Na^+ for K^+ raises the polymorphic transition pressure (P_{tr}^m) of KCl in an almost linear fashion (as a function of m/o NaCl). On the other hand, this cationic substitution lowers the polymorphic transition volume (ΔV_{tr}). A distinct trend is seen from comparison of the results from this study with the results from a similar study by Darnell *et al.* (*6*) on the KCl–RbCl system; viz., substitution of the larger Rb^+ ion in KCl lowers the polymorphic transition pressure (P_{tr}^m) but increases the transition volume (ΔV_{tr}). In contrast, the reverse effect is noted in P_{tr}^m and ΔV_{tr} upon the substitution of the smaller Na^+ cation in KCl. In particular, it is noted in the KCl–NaCl system that $\Delta V_{tr} \to 0$ when $X(NaCl) \to 1$. Thus for thermodynamic reasons, the pressure induced polymorphic transition in solid solutions of KCl–NaCl fails to occur at high concentrations of NaCl. These results give some clue or explanation why a transition is not observed in NaCl in the pressure region of 15–30 kb, such as is observed in the case of RbCl at a pressure of 5 kb and in KCl at 20 kb. NaCl behaves much differently from the latter two salts in its $Fm3m \rightleftarrows Pm3m$ transition. Such a transition has been observed in NaCl by Bassett and Takahashi (*17*) at a much higher pressure of 300 kb. At this extreme pressure the volume change for this $Fm3m \to Pm3m$ transition in NaCl behaves in a normal manner.

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