

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  $\Delta V_{tr}$  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<sup>2</sup> (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,  $t < 300^\circ$ , (b) the region of extensive solid-solid solubility, 300–600°, and (c) the region of complete miscibility,  $t > 600^\circ$ . 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

<sup>2</sup> 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  $\Delta V_{tr}$  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  $\Delta V$  and  $\Delta S$  of formation of this solid solution (11).

In the third case, as illustrated by temperatures above 600°,<sup>3</sup>  $P_{tr}^m$  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

<sup>3</sup> 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.