

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.

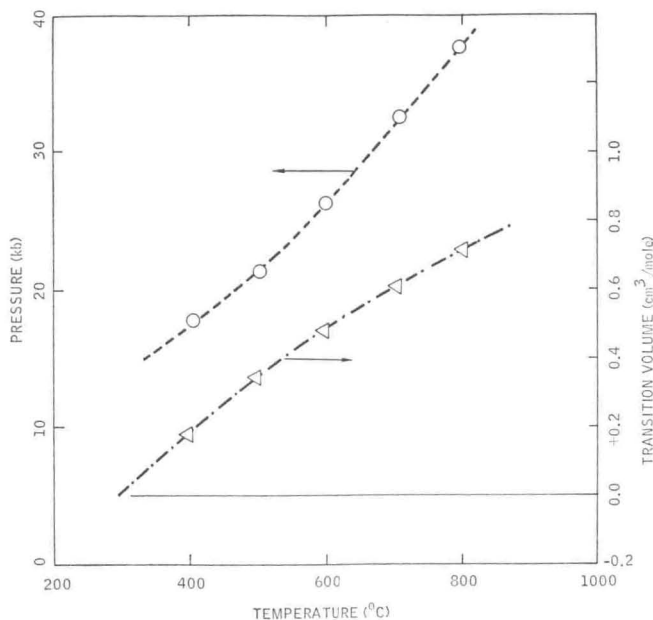


FIG. 4. Transition pressure (P_{tr}^m) and transition volume (ΔV_{tr}) obtained from extrapolation of the curves P_{tr}^m vs X (NaCl) and ΔV_{tr} vs X (NaCl) to X (NaCl) = 1 at the isotherms 400°–800°.

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 ($> 600^\circ$) 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 $\Delta V_{\text{tr}} \rightarrow 0$ when $X(\text{NaCl}) \rightarrow 1$. 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 $Fm3m \rightleftharpoons Pm3m$ 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 $Fm3m \rightarrow Pm3m$ transition in NaCl behaves in a normal manner.

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