

volume between these two polymorphs decreases with increasing temperature for the solid solutions and for the pure salts (9).

The P - V curves for these binary solid solutions of the salts KCl-RbCl and KCl-KBr are similar to the P - V curves found for the component salts. A typical pressure-volume curve for these solid solutions is shown in Fig. 1 for the salt $K(\text{Cl}_{0.50}\text{Br}_{0.50})$ at 500°C . In general, for all compositions examined, we find that the P - V curves for these solid solutions more closely approach the shape of the P - V curves of the pure component salts [and also to the "idealized" curve depicted by Jayaraman *et al.* (28)] at higher temperatures. This can be seen in Fig. 4, where the average width of

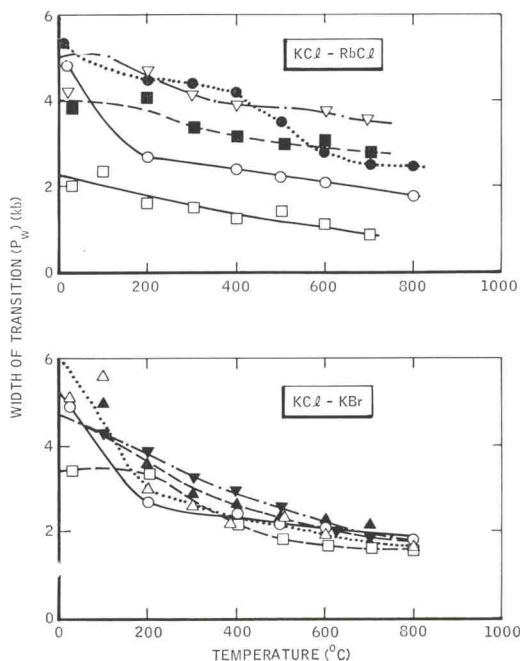


FIG. 4. Width of the polymorphic transition (P_w) vs temperature. In the KCl-RbCl system: KCl \circ - \circ , $(\text{K}_{0.75}\text{Rb}_{0.25})\text{Cl}$ ∇ - ∇ , $(\text{K}_{0.50}\text{Rb}_{0.50})\text{Cl}$ \blacksquare - \blacksquare , $(\text{K}_{0.25}\text{Rb}_{0.75})\text{Cl}$ \bullet - \bullet , RbCl \square - \square . In the KCl-KBr system: KCl \circ - \circ , $\text{K}(\text{Cl}_{0.75}\text{Br}_{0.25})$ \blacktriangle - \blacktriangle , $\text{K}(\text{Cl}_{0.50}\text{Br}_{0.50})$ \triangle - \triangle , $\text{K}(\text{Cl}_{0.25}\text{Br}_{0.75})$ \blacktriangledown - \blacktriangledown , KBr \square - \square .

the transition (P_w) in these salts is shown as a function of temperature. Indeed, at 700°C the width of the transition of the solid solutions in the KCl-KBr system is almost identical to P_w for the component salts. However, P_w for solid solutions of KCl-RbCl is still considerably greater than for KCl and RbCl, even at 800°C .

Further insight into the polymorphic transition in these solid solutions may be gained from examination of the pressure-composition (P - x) diagrams at constant temperature. In Fig. 5 the width of the transition P_w is shown as a function of composition at three temperatures, 200, 500, and 800°C for the system KCl-RbCl. Similarly, Fig. 6 shows the P - x diagram for the KCl-KBr system at a temperature of 500°C .

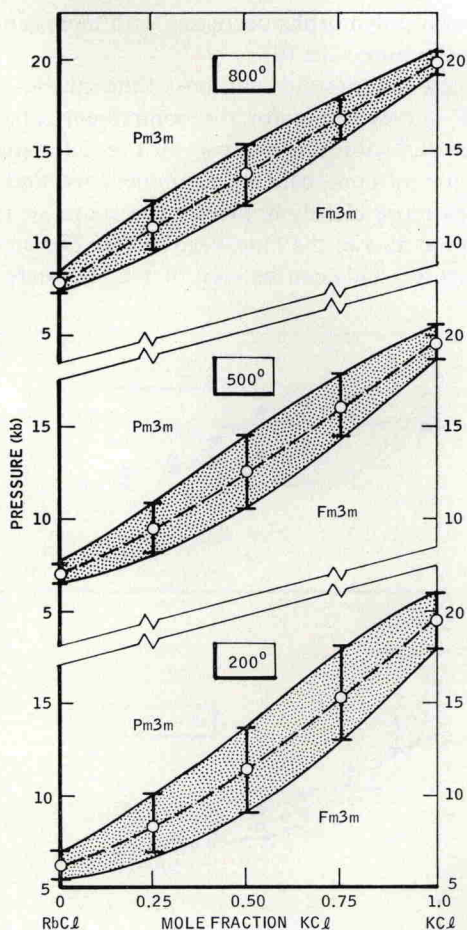


FIG. 5. Isothermal pressure-composition diagram for the KCl-RbCl system at 200°, 500°, and 800°C.

The larger pressure interval for the polymorphic transition in these solid solutions, in comparison to the interval found for the pure salts, may be due in part to a greater hysteresis effect in the solid solutions. However, it is ~~likely~~ likely that this larger transition pressure interval is due in part to the finite width of the solid-solid transition in this binary system (29, 30). In a P - x diagram such as that illustrated by Figs. 5 and 6 a transition of this type would be outlined by two subsolidus² curves, analogous to the solidus-liquidus curves found in the constant pressure T - x diagrams for these systems (23). It is not felt, however, that the subsolidus curves can be obtained by subtraction of the pressure interval due to hysteresis in the case of the pure salts from the pressure interval found in the solid solutions. This is primarily because hysteresis for the solid solutions may be different than for the pure salts. It would

² Using the terminology of Ricci (31) phase transitions occurring at temperatures below the liquidus-solidus curves are called "subsolidus."