



FIG. 1. P - V curve for $K(\text{Cl}_{0.5}\text{Br}_{0.5})$ at 500°C . Upper curve is for compression; lower curve for decompression.

and decompression, i.e., from Fig. 1,

$$P_{\text{tr}} = \frac{P_a + P_d}{2}. \quad (2)$$

This is similar to the technique employed by Jayaraman *et al.* (28). In the case of the pure salts we find that an average of the midpoint of the transition pressure for the compression and decompression yields essentially the same value for P_{tr} , i.e., with reference to Fig. 1, $(P_a + P_d)/2 \cong (P_b + P_c)/2$. Although the transition in a solid solution at constant temperature from thermodynamic considerations should occur over a finite pressure interval (29, 30), we have considered the midpoint of the

transition pressure interval in these solid solutions as though it were an equilibrium transition pressure of a pure component. With reference to Fig. 1, the midpoint of the transition pressure upon compression, P_b , is $(P_a + P_c)/2$; for decompression it is equal to $(P_d + P_f)/2$. Averaging these midpoints we obtain the mean transition pressure P_{tr}^m , where

$$P_{tr}^m = \frac{P_b + P_e}{2}. \quad (3)$$

The "width" of the transition pressure interval is given by $P_c - P_a$ and $P_d - P_f$ (see Fig. 1) for the compression and decompression processes, respectively. Ideally for the pure salts this width should be equal to zero. In actual practice this is not found to be the case even at temperatures approaching the melting point (9). Hysteresis and pressure gradients within the sample contribute to the width of this pressure interval in the pure salts; in the solid solutions there may also be a broadening since the transition may have finite width. The "width" of this transition (P_w) was determined for both the pure salts and the solid solutions from

$$P_w = \frac{(P_c - P_a) + (P_d - P_f)}{2}, \quad (4)$$

with pressure-volume coordinates defined in Fig. 1.

The volume change associated with this solid-solid phase transition was obtained from extrapolation of the pre- and post-transition segments of the P - V curves (Fig. 1) to the pressures P_b and P_e . These points represent the midpoint of the transition pressure in the compression and decompression processes, respectively. Thus upon compression, $\Delta V_{\text{compression cycle}} = V_{b''} - V_{b'}$; upon decompression, $\Delta V_{\text{decompression cycle}} = V_{e'} - V_{e''}$. The average volume change for the transition (ΔV_{tr}) was determined from

$$\Delta V_{tr} = \pm \frac{[(V_{e'} - V_{e''}) - (V_{b''} - V_{b'})]}{2}, \quad (5)$$

where the positive sign applies to $\Delta V_{tr}(Pm3m \rightarrow Fm3m)$ and the negative sign to the reverse reaction.

III. RESULTS AND DISCUSSION

The mean pressure (P_{tr}^m) at which solid solutions of salts in the KCl-RbCl and KCl-KBr systems undergo a polymorphic transition was determined at approximately 100° intervals from room temperature to 700°C (800°C in some cases). The results for the salts $(K_{0.75}Rb_{0.25})Cl$, $(K_{0.50}Rb_{0.50})Cl$, $(K_{0.25}Rb_{0.75})Cl$, $K(Cl_{0.75}Br_{0.25})$, $K(Cl_{0.50}Br_{0.50})$, and $K(Cl_{0.25}Br_{0.75})$ are shown in Fig. 2. For comparison, the transition pressures (P_{tr}) for the pure salts KCl, RbCl, and KBr (9) are also shown in Fig. 2. The mean transition pressure (P_{tr}^m) for these solid solutions, as was found in the case for the pure salts (9), is a linear function of the temperature over the interval 200°C to 800°C. The least-squares fit of these data for each of these solid solutions is given in the form

$$P_{tr}^m(kb) = a + bt \text{ (}^\circ\text{C)}, \quad (6)$$

where P_{tr}^m is the midpoint of the polymorphic transition as defined by Eq. (3); a and b are constants. The coefficient b is of particular interest since it gives the temperature