

FIG. 2. Transition pressure (P_{tr}^m) vs temperature for the polymorphic phase change in the systems KCl-RbCl and KCl-KBr.

variation of the mean transition temperature, i.e., $b = dP_{tr}^m/dT$. Values of a and b for these solid solutions and for the component salts (9) are given in Table 1. In each case this transition pressure vs temperature equation has been extrapolated (dashed line in Fig. 2) to obtain the transition pressure at 25°C. In this experimental technique we think the values of the transition pressures obtained at 25°C by this extrapolation are more reliable than our directly determined values of P_{tr}^m at 25°C.

TABLE 1

CONSTANTS FOR THE TEMPERATURE DEPENDENCE OF THE POLYMORPHIC TRANSITION PRESSURE [$P_{tr}^m(\text{kb}) = a + bt(^\circ\text{C})$] AND THE POLYMORPHIC TRANSITION VOLUME [$V_{tr}(\text{cm}^3/\text{mole}) = c + dt(^\circ\text{C})$] FOR SALTS IN THE SYSTEMS KCl-RbCl AND KCl-KBr

Salt	a (kb)	$b \times 10^3$ (kb/deg)	c (cm^3/mole)	$d \times 10^3$ ($\text{cm}^3/\text{mole}/\text{deg}$)
KCl ^a	19.55 ± 0.13	-0.02 ± 0.26	-4.13 ± 0.01	0.83 ± 0.18
(K _{0.75} Rb _{0.25})Cl	15.15 ± 0.19	$+1.93 \pm 0.35$	-4.49 ± 0.12	1.04 ± 0.22
(K _{0.50} Rb _{0.50})Cl	10.40 ± 0.01	$+4.00 \pm 0.04$	-4.96 ± 0.10	1.55 ± 0.21
(K _{0.25} Rb _{0.75})Cl	7.84 ± 0.02	$+3.71 \pm 0.43$	-5.70 ± 0.07	2.10 ± 0.14
RbCl ^a	5.61 ± 0.14	$+2.80 \pm 0.30$	-6.96 ± 0.11	2.88 ± 0.27
K(Cl _{0.75} Br _{0.25})	21.23 ± 0.17	-1.37 ± 0.35	-3.90 ± 0.04	0.73 ± 0.09
K(Cl _{0.50} Br _{0.50})	20.76 ± 0.14	-1.54 ± 0.29	-3.89 ± 0.08	0.73 ± 0.17
K(Cl _{0.25} Br _{0.75})	19.00 ± 0.15	-0.90 ± 0.33	-3.78 ± 0.12	0.47 ± 0.21
KBr ^a	18.02 ± 0.28	-1.19 ± 0.49	-4.19 ± 0.11	0.87 ± 0.20

^a Darnell and McCollum, Ref. (9).

This is because the much larger frictional and hysteresis effects at 25°C (as compared to $t > 200^\circ\text{C}$) lead to a greater uncertainty in P_{tr}^m than arises from this extrapolation of the high temperature data. In the case of KCl, RbCl, and KBr the value of P_{tr} at 25°C from a similar extrapolation (9) was found to be in good agreement with the transition pressure reported by other workers using different experimental techniques.

The volume change (ΔV_{tr}) of the polymorphic transition in these solid solutions was also measured over the temperature interval 25°C to about 800°C (Fig. 3). Here also, as in the case of P_{tr}^m , only the data above 200°C have been used. At lower

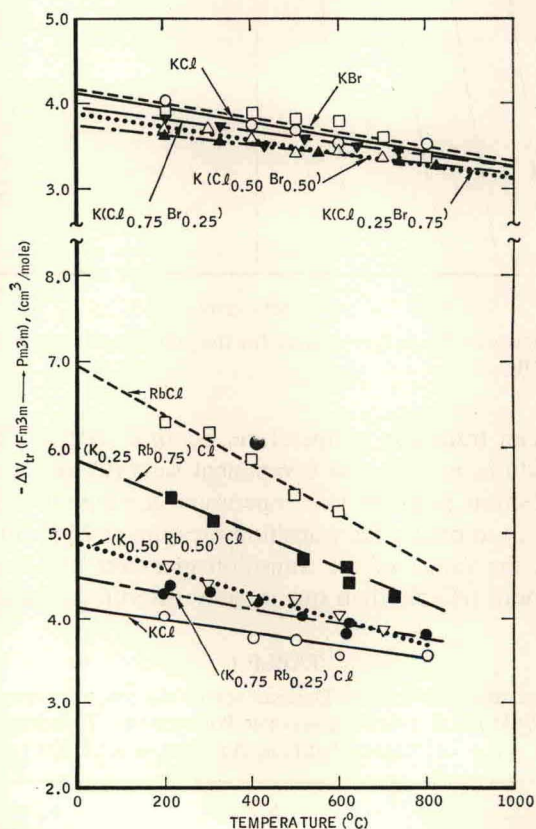


FIG. 3. Volume change of the polymorphic transition for salts in the systems KCl-RbCl and KCl-KBr.

temperatures, where frictional effects, hysteresis, and sluggishness of the transition are more pronounced, it is difficult to obtain a reliable extrapolation of the pre- and post-transition curve to the midpoint of the transition. The transition volume at a given temperature t (°C) is represented by

$$\Delta V_{tr} (\text{cm}^3/\text{mole}) = c + dt (\text{°C}), \quad (7)$$

where c and d are constants. Values of c and d obtained by least-squares treatment of the data are given in Table 1. As can be seen from Fig. 3, the difference in specific