Fig. 2. *PV* diagram for the rubidium halides: □ — melting point data of Clark (1959). ■ — melting point data of Pistorius (1965, 1966). ○ — Fm3m ⇄ Pm3m transition, this work.

served in KF at pressures up to 45 kb and at temperatures up to 800°C.

As in the case of most solid–solid phase transitions[21] these salts also show a hysteresis effect. The width of the hysteresis loop is, in general, less than one kilobar at temperatures greater than 200°C, and becomes larger and less reproducible at temperatures below 200°C. We have assumed that the equilibrium transition pressure is the average of the transition pressures obtained on compression and decompression. In all cases, the equilibrium transition pressure appears, within the experimental accuracy of these data, to be a linear function of the temperature over the interval 200–700°C. These P_{tr} data were treated by method of least squares to obtain the transition pressure as a function of temperature in

the form

$$P_{tr}(kb) = a + bt \qquad (1)$$

where P_{tr} is the Fm3m $\rightleftarrows$ Pm3m transition pressure at a given temperature t (°C). Data for the constants a and b are given in Table 1. The constant b is of particular significance since $b = dP/dT$. The values for the transition pressure at 25°C reported in Table 2 were obtained from extrapolation of the high temperature data, by the use of equation (1).

The transition volumes* (ΔV_{tr}, Fm3m $\rightarrow$ Pm3m) for KCl, KBr and KI at temperatures between 200–800°C are shown in Fig. 3. Similarly, ΔV_{tr} for RbF, RbCl, RbBr and RbI are shown in Fig. 4. The volume change (ΔV_{tr}) appears to be a linear function of temperature at temperatures above 200°C. These data were also treated by method of least squares to obtain the transition volume as a function of temperature in the form

$$\Delta V_{tr}(\text{cm}^3/\text{mole}) = c + dt. \qquad (2)$$

where ΔV_{tr} is the transition volume at a given temperature t (°C). Values for the constants c and d are given in Table 1. The transition volumes at 25°C reported in Table 3 were obtained from an extrapolation of the high tem-

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*The transition volume vs. temperature data shown in Figs. 3 and 4 are not at constant pressure (except in the special case of KCl where $dT/dP \approx 0$) but are at pressures corresponding to the temperatures along the Fm3m $\rightleftarrows$ Pm3m phase boundary.
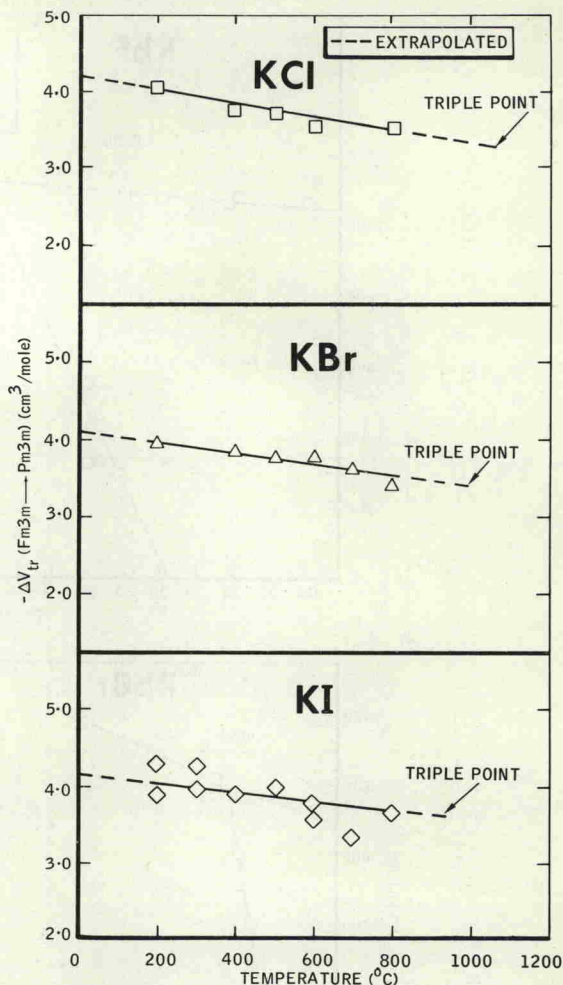

Fig. 3. ΔV(Fm3m $\rightarrow$ Pm3m) vs. T for KCl, KBr and KI.

Table 1. Constants for the temperature dependence of the Fm3m $\rightleftarrows$ Pm3m transition pressure $[P_{tr}(kb) = a + bt]$ and the transition volume Fm3m $\rightarrow$ Pm3m $[\Delta V_{tr}(\text{cm}^3/\text{mole}) = c + dt]$ in the potassium and rubidium halides

Salt	a (kb)	$b \times 10^3$ (kb/deg)	c (cm³/mole)	$d \times 10^3$ (cm³/mole/deg)
KCl	$19·55 \pm 0·13$	$-0·015 \pm 0·256$	$-4·13 \pm 0·01$	$0·830 \pm 0·176$
KBr	$18·02 \pm 0·28$	$-1·186 \pm 0·485$	$-4·19 \pm 0·11$	$0·869 \pm 0·201$
KI	$18·35 \pm 0·20$	$-3·223 \pm 0·387$	$-4·44 \pm 0·15$	$1·211 \pm 0·295$
RbF	$34·37 \pm 0·38$	$+3·723 \pm 0·710$	$-1·84 \pm 0·29$	$0·445 \pm 0·513$
RbCl	$5·61 \pm 0·14$	$+2·800 \pm 0·296$	$-6·96 \pm 0·11$	$2·880 \pm 0·269$
RbBr	$4·88 \pm 0·06$	$+1·371 \pm 0·124$	$-7·47 \pm 0·18$	$1·597 \pm 0·366$
RbI	$3·64 \pm 0·05$	$+1·400 \pm 0·115$	$-8·15 \pm 0·10$	$1·920 \pm 0·236$