FIG. 6. Isothermal pressure–composition diagram for the KCl–KBr system at 500°C.

appear, however, that upper and lower limits of the subsolidus curves for this transition would be established by the P–x curves in Figs. 5 and 6.

The results from this study suggest that the pressure-induced transition in these solid solutions occurs with a change in structure from the rock salt form to the CsCl form. This would seem reasonable because of the similarity of these pressure-induced phase changes in these solid solutions to the polymorphic transitions found in the component salts (9). The latter are known from high pressure X-ray diffraction studies to undergo the $Fm3m \rightleftarrows Pm3m$ phase change (32, 33). Also by analogy, Wood and co-workers (17, 18) have shown by X-ray diffraction that the temperature-induced (atmospheric pressure) transition in solid solutions of CsCl with RbCl and with CsBr is of the type $Pm3m \rightleftarrows Fm3m$. As mentioned above, the solid solutions of the salts KCl–RbCl and KCl–KBr in their ordinary $Fm3m$ form at atmospheric pressure are approximately ideal in their behaviour.[3] The relatively narrow pressure interval between the upper and lower subsolidus curves in Figs. 5 and 6, particularly at high temperatures, suggests that the high-pressure polymorph is also very nearly an ideal solid solution.

The thermodynamic properties of this polymorphic transition in these solid solutions are calculated, as an approximation, by treating the midpoint of the transition pressure (P_{tr}^m) as if it were an equilibrium transition pressure (P_{tr}) for a pure component. Data given for the transition pressure (P_{tr}^m) and the volume change (ΔV_{tr}) in Columns 2 and 4, respectively, of Table 2 are used to calculate the $P\Delta V$ work necessary to carry out this transition. Similarly the temperature derivative of the mean transition pressure (dP_{tr}^m/dT) given by constant b in Table 1 was used in conjunction with ΔV_{tr} to calculate ΔS_{tr}^m from the Clausius–Clapeyron relation. The values for $P_{tr}^m \Delta V_{tr}$, $T\Delta S_{tr}^m$, and ΔE_{tr}^m for the hypothetical phase transition solid solution (I) → solid solution (II), carried out isothermally at the mean transition pressure P_{tr}^m, are given in Table 2 and are also shown as a function of the mole fraction of KCl in Fig. 7.

Taking KCl as a reference, the effect of ionic substitution upon the properties of this polymorphic transition can now be examined. Formation of solid solutions by

[3] The solid solutions of these salts are considered to be approximately ideal at ambient pressure since their ΔV and ΔH of formation from the pure component salts are not large (34–37).

TABLE 2

THERMODYNAMIC PROPERTIES OF THE POLYMORPHIC TRANSITION IN THE
KCl–RbCl AND KCl–KBr SYSTEMS AT 298°K

| Salt	P_{tr}^m (kb)	dT/dP_{tr}^m (°C/kb)	$-\Delta V_{tr}$ (cm³/mole)	$-P_{tr}^m\Delta V_{tr}$ (cal/mole)	$T\Delta S_{tr}^m$ (cal/mole)	$-\Delta E_{tr}^m$ (cal/mole)
KCl	19.55 ± 0.13	$-62{,}500$	4.11 ± 0.10	1920	0	1920 ± 150
$(K_{0.75}Rb_{0.25})Cl$	15.19 ± 0.19	$+520$	4.46 ± 0.12	1580	-61	1519 ± 250
$(K_{0.50}Rb_{0.50})Cl$	10.50 ± 0.01	$+250$	4.91 ± 0.10	1230	-150	1080 ± 100
$(K_{0.25}Rb_{0.75})Cl$	7.94 ± 0.02	$+269$	5.63 ± 0.07	1080	-144	936 ± 50
RbCl	5.68 ± 0.14	$+357$	6.95 ± 0.11	945	-138	807 ± 150
$K(Cl_{0.75}Br_{0.25})$	20.5 ± 0.2	-730	3.96 ± 0.2	1940	$+39$	1980 ± 300
$K(Cl_{0.50}Br_{0.50})$	20.72 ± 0.14	-650	3.87 ± 0.08	1920	$+40$	1960 ± 150
$K(Cl_{0.25}Br_{0.75})$	19.7 ± 0.2	-1100	3.95 ± 0.2	1860	$+26$	1896 ± 300
KBr	17.99 ± 0.28	-843	4.17 ± 0.11	1790	$+35$	1825 ± 300
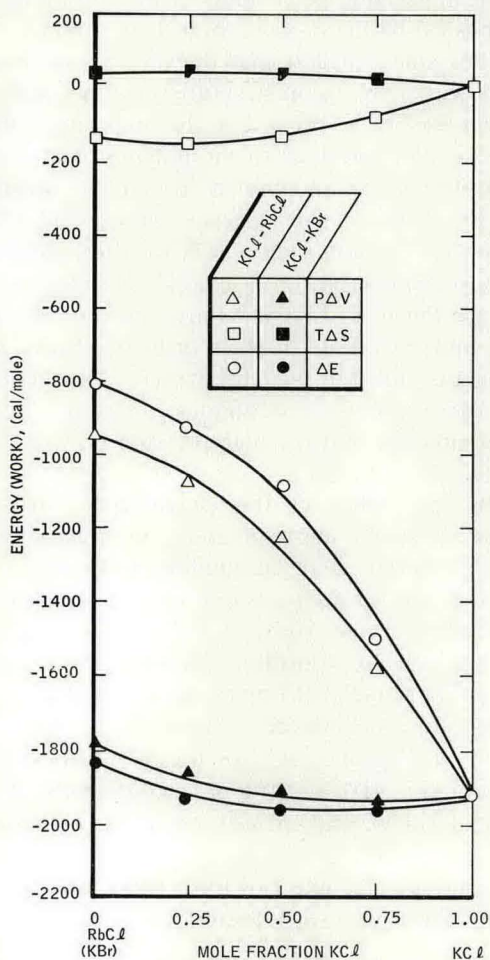
FIG. 7. Variation of $P_{tr}^m\Delta V$, $T\Delta S_{tr}^m$, and ΔE_{tr}^m with mole fraction KCl in the systems KCl–RbCl and KCl–KBr at 298°K.