Ion Exchange in Fused Salts. Part VII.† Ion-exchange Isotherms for Thallium(I)–Potassium and Rubidium–Potassium on Crystalline Zirconium Phosphate in Molten Thallium Nitrate–Potassium Nitrate and Rubidium Nitrate–Potassium Nitrate Mixtures at 360 °C

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Ion-exchange isotherms for Tl^+–K^+ and Rb^+–K^+ on crystalline zirconium phosphate in molten $Tl[NO_3]$–$K[NO_3]$ and $Rb[NO_3]$–$K[NO_3]$ mixtures are almost fully reversible processes which occur in several steps either *via* a two-phase transition or a solid–solution mechanism. There is a strong dependence of the gradients of the isotherms on the polarisability of the exchanging cations, and some of the equilibrium constants have been calculated.

PREVIOUS ion-exchange experiments of Li^+, Na^+, and K^+ on amorphous and crystalline zirconium phosphate in molten salts [1,2] have demonstrated that the selectivity of the exchanger depends on the size of the exchanging cations. Indeeds the selectivity orders are reversed in aqueous and in anhydrous media.[1]

In order to ascertain the influence of the cation polarisability on the coulombic interaction between the fixed groups and the counter ions, it seemed of interest to investigate the ion-exchange behaviour of rubidium(I) and thallium(I) ions, which have the same crystalline ionic radius but very different polarisability. This paper reports the K^+–Rb^+ and K^+–Tl^+ ion-exchange isotherms of crystalline zirconium phosphate in molten $K[NO_3]$–$Rb[NO_3]$ and $K[NO_3]$–$Tl[NO_3]$ mixtures at 360 °C.

EXPERIMENTAL

Chemicals.—All reagents were Merck ' pro-analysis ' products, except $K[NO_3]$ which was Erba RP-ACS.

Crystalline zirconium phosphate was obtained by the direct precipitation method.[3] The dipotassium form was prepared by direct titration of the hydrogen form of the exchanger with 0.1 N K[OH]–KCl solutions followed by dehydration of the product at 300 °C. The dithallium and dirubidium forms were prepared by percolating molten $Tl[NO_3]$ or $Rb[NO_3]$ through the dipotassium form at 360 °C.

Apparatus and Procedures.—The apparatus and procedures employed to obtain the ion-exchange isotherms were as reported previously.[4]

Potassium and rubidium ions were determined on a Varian-Tecktron A.A. 120 atomic-absorption spectrophotometer. Thallium(I) was determined by potentiometric titration.[5] Phosphate ion was determined according to ref. 6. *X*-Ray diffraction patterns and photographs were obtained on a Philips diffractometer and a Philips camera (type PW 1026), respectively, using nickel-filtered Cu-K_α radiation.

RESULTS AND DISCUSSION

Figure 1 shows the K^+–Tl^+(*a*) and K^+–Rb^+(*b*) ion-exchange isotherms at 360 °C in molten $K[NO_3]$–$Tl[NO_3]$ and $K[NO_3]$–$Rb[NO_3]$ mixtures respectively. Since Rb^+ and Tl^+ possess very similar crystalline ionic radii,[7] the large changes in ion-exchange isotherms between the two ions must be ascribed to differences in cation polarisability. The two isotherms are treated separately for clarity.

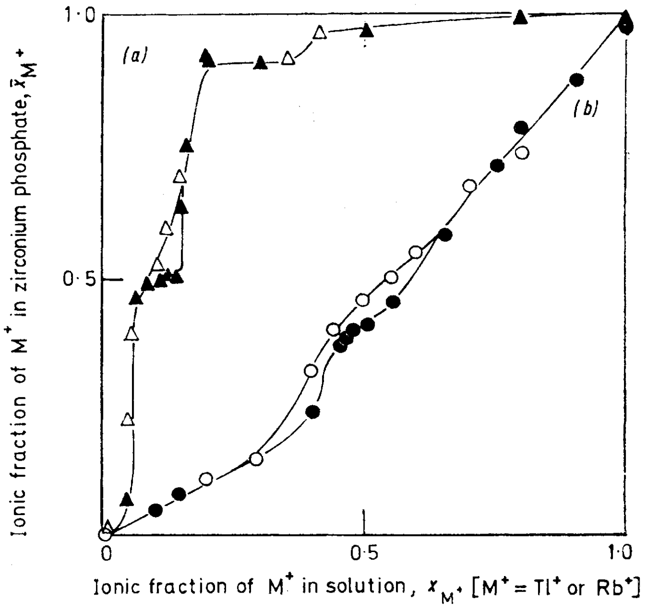

FIGURE 1 Ion-exchange isotherms for K^+–Tl^+ (*a*) and K^+–Rb^+ (*b*) on crystalline zirconium phosphate in $K[NO_3]$–$Tl[NO_3]$ and $K[NO_3]$–$Rb[NO_3]$ mixtures at 360 °C: (△) $K^+ \longrightarrow \overline{Tl}^+$; (▲) $Tl^+ \longrightarrow \overline{K}^+$; (○) $K^+ \longrightarrow \overline{Rb}^+$; (●) $Rb^+ \longrightarrow \overline{K}^+$

(*a*) K^+–Tl^+ *Ion-exchange Isotherms*.—The shapes of the K^+–Tl^+ ion-exchange isotherms [Figure 1(*a*)] show that, at 360 °C, crystalline zirconium phosphate strongly prefers Tl^+, which has a larger ionic radius (1.47 Å) compared to K^+ (1.33 Å). From Figure 1(*a*) it can also be inferred that the K^+–Tl^- ion-exchange processes are fully reversible, except in the range $\bar{x}_{Tl}$‡ 0.45—0.6, where a small hysteresis loop occurs.

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† Part VI is ref. 2.

‡ $\bar{x}_{Tl}$ is the ionic fraction of Tl in the exchanger.

[1] G. Alberti, S. Allulli, and A. Conte, *J. Chromatog.*, 1966, **24**, 148.

[2] S. Allulli, A. La Ginestra, and N. Tomassini, *J. Inorg. Nuclear Chem.*, 1974, **36**, 3839.

[3] G. Alberti and E. Torracca, *J. Inorg. Nuclear Chem.*, 1968, **30**, 317.

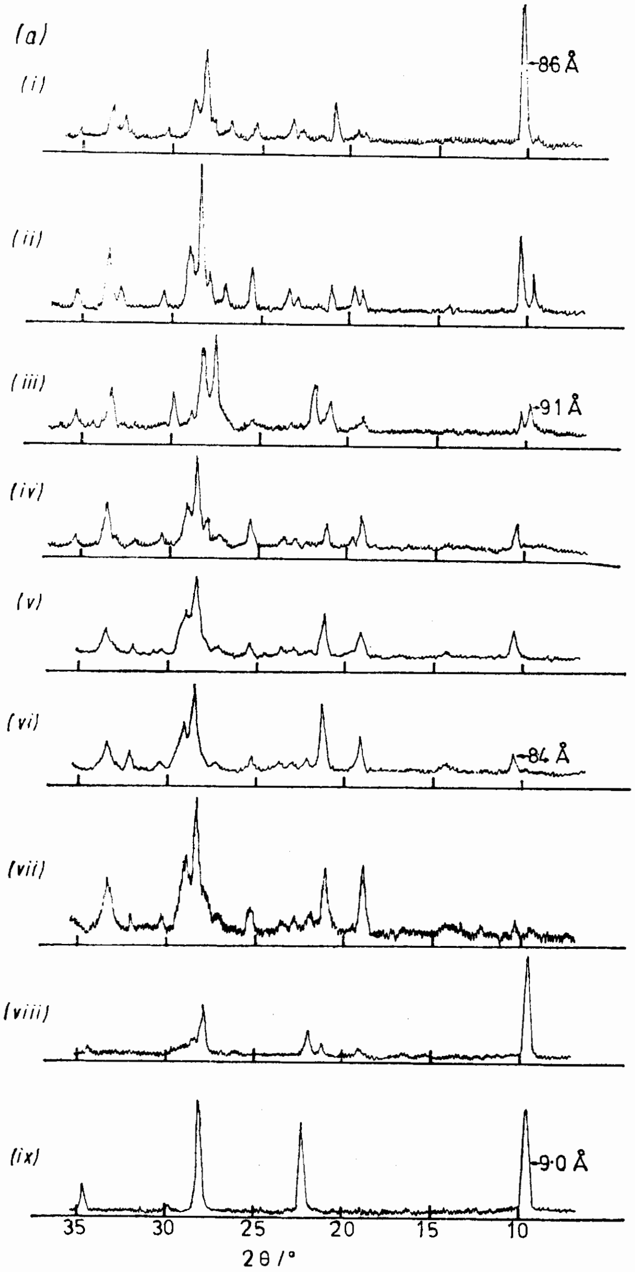
[4] G. Alberti, S. Allulli, and G. Cardini, *J. Chromatog.*, 1969, **45**, 298.

[5] A. I. Vogel, 'A Text-Book of Quantitative Inorganic Analysis,' 3rd edn., Longmans, London, 1961.

[6] D. N. Bernart and A. R. Wreath, *Analyt. Chem.*, 1955, **27**, 440.

[7] ' Handbook of Chemistry and Physics,' ed. R. C. Weast, The Chemical Rubber Co., Cleveland, Ohio, 1971, p. 44128.

The ion-exchange isotherms had three vertical portions ($\bar{x}_{Tl}$ 0—0.48, 0.60—0.90, and 0.90—1.0) and two plateaux at $\bar{x}_{Tl}$ *ca.* 0.50 and 0.90 respectively, the former of which holds only for the $Tl^+ \longrightarrow \overline{K}^+$ process.[§] It is to be noted that, owing to the occurrence of the first ($\bar{x}_{Tl}$0 —0.48) vertical portion of the isotherms at very low mole fraction of thallium ions in the solvent ($\bar{x}_{Tl}$ *ca.* 0.05), in calculating the equilibrium values it is necessary to take into account the contribution of the ions entering, or leaving, the exchanger. This means that, as for the ion-exchange processes in aqueous solutions, the final value of the solvent mole fraction depends on the loading of the exchanger and cannot be considered as a buffered value, as was believed to be the case for highly ionic media such as molten nitrates.[4]



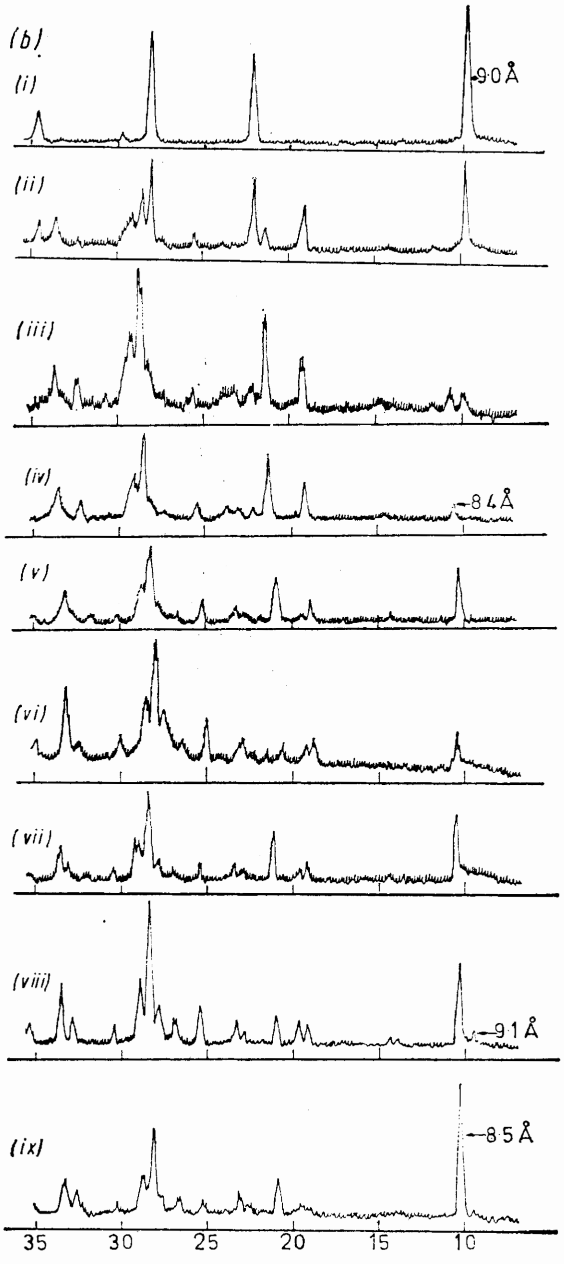


FIGURE 2 X-Ray diffraction patterns of several samples from the $Tl^+ \longrightarrow \overline{K}^+$ (*a*) and $K^+ \longrightarrow \overline{Tl}^+$ processes (*b*) in molten $K[NO_3]$–$Tl[NO_3]$ mixtures at 360 °C. Sensitivity 2×10^3 counts s^{-1}. (*a*) $\bar{x}_{Tl} = 1.00$ (*i*), 0.98 (*ii*), 0.92 (*iii*), 0.71 (*iv*), 0.62 (*v*), 0.49 (*vi*), 0.45 (*vii*), 0.06 (*viii*), and 0.00 (*ix*); (*b*) $\bar{x}_{Tl} = 0.00$ (*i*), 0.23 (*ii*), 0.38 (*iii*), 0.55 (*iv*), 0.7 (*v*), 0.83 (*vi*), 0.90 (*vii*), 0.97 (*viii*), and 1.00 (*ix*)

In order to assess the K^+–Tl^+ ion-exchange behaviour, X-ray diffraction spectra were examined (Figure 2). Two phases, the dipotassium and thallium–potassium forms of zirconium phosphate, are present in the range

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[§] The convention $Tl^+ \longrightarrow \overline{K}^+$ and $K^+ \longrightarrow \overline{Tl}^+$ represents Tl^+ replacing K^+ in the exchanger and *vice versa*.

$\bar{x}_{\text{Tl}}$ 0—0.5. These (as well as the other solid phases found in the ion-exchange isotherms) will be identified by their counter ion composition and interlayer distance, namely $\overline{\text{KK}}$ (9.1 Å) and $\overline{\text{KTl}}$ (8.4 Å) respectively.

In the range $\bar{x}_{\text{Tl}}$ 0.6—0.9, there were only small variations in the *X*-ray diffraction patterns in both intensity and position of the reflections The *d* spacing of the zirconium layer ranged from 8.4 to 8.5 Å notwithstanding the large variation in the Tl^+ loading. Thus, Tl^+ can enter the $\overline{\text{TlK}}$ (8.4 Å) phase [or K^+ the $\overline{\text{K}_{0.2}\text{Tl}_{1.8}}$ (8.5 Å) phase], without a drastic rearrangement of the lattice structure, to form a solid solution. Samples in the range $\bar{x}_{\text{Tl}}$ 0.9—0.98 revealed the appearance of a new crystalline phase having an interlayer distance (9.1 Å) higher than that of the 8.5 Å phase. *X*-Ray diffraction patterns of the zirconium phosphate fully converted into the thallium form clearly showed that the *d* spacing of 9.1 Å does not belong to the $\overline{\text{TlTl}}$ phase, which has an interlayer distance of 8.6 Å.

The assignment of the reflection at $2\theta = 9.7$ (9.1 Å) is not straightforward since it appears unlikely that it belongs to a $\overline{\text{Tl}_x\text{K}_y}$ phase owing to the interlayer distances of 8.4 and 8.6 Å for the $\overline{\text{Tl–K}}$ and $\overline{\text{Tl–Tl}}$ forms, respectively. As a tentative explanation, we suggest that at these Tl^+ loadings the $\overline{\text{K}_{0.2}\text{Tl}_{1.8}}$ (8.5 Å) phase segregates into a dithallium and a dipotassium phase which has an interlayer distance very close to the pure $\overline{\text{KK}}$ (9.0 Å) phase.

A general trend in the *X*-ray diffraction patterns of all the samples investigated is the low-intensity value * found for the reflections at $2\theta = 10.5$ which correspond to the interlayer distance of the $\overline{\text{KTl}}$ form and/or the solid solutions in the range $\bar{x}_{\text{Tl}}$ 0.5—0.9. This fact seems to be related to the presence in the exchanger of two unlike cations having large differences in their ionic radii and/or polarisability; *X*-ray patterns of the $\overline{\text{HCs}}\cdot 2\text{H}_2\text{O}$ and $\overline{\text{HRb}}\cdot 1.5\text{H}_2\text{O}$ forms [8] support this hypothesis. The weakening of the 002 reflection in the heteroionic forms may be due to a disordered array of the zirconium atoms caused by faulty balancing of the van der Waals forces between the layers.

The forward and reverse K–Tl exchange can be summarised as in (1). Care must be taken in making

$$\underset{(9.0\ \text{Å})}{\overline{\text{KK}}} \underset{+\,0.95\ \text{K}^+}{\overset{+\,0.95\ \text{Tl}^+}{\rightleftharpoons}} \underset{(8.4\ \text{Å})}{\overline{\text{K}_{1.05}\text{Tl}_{0.95}}} \underset{+\,0.85\ \text{K}^+}{\overset{+\,0.85\ \text{Tl}^+}{\rightleftharpoons}}$$

$$\underset{(\text{solid soln. } 8.5\ \text{Å})}{\overline{\text{K}_{0.2}\text{Tl}_{1.8}}} \underset{+\,0.2\ \text{K}^+}{\overset{+\,0.2\ \text{Tl}^+}{\rightleftharpoons}} \underset{(8.6\ \text{Å})}{\overline{\text{TlTl}}} \quad (1)$$

thermodynamic calculations on the processes reported above. In fact, in the second step we have a hysteresis loop for a small extent of the exchange (*ca.* 20%) and in the third step we have the occurrence of the 9.1 Å phase (see Figure 2) the chemical composition of which has not yet been clearly determined.

Since the crystalline phases $\text{Zr[Tl(PO}_4)]_2$ and $\text{ZrKTl(PO}_4)_2$ have not yet been reported in the literature, the *X*-ray powder patterns of these compounds are given in the Table.

TABLE

X-ray powder photographs of some salt forms of crystalline zirconium phosphate

$\overline{\text{Tl–Tl}}$		$\overline{\text{K–Tl}}$		$\overline{\text{Rb–Rb}}$		$\overline{\text{K}_{1.2}\text{–Rb}_{0.8}}$	
d(Å)	*i*	*d*(Å)	*i*	*d*(Å)	*i*	*d*(Å)	*i*
8.60	100	8.40	20	9.11	55	9.11	5
6.43	5	6.43	5	4.57	10	8.20	70
5.21	5	6.10	5	4.10	45	7.69	5
4.62	10	6.42	40	3.23	100	6.10	5
4.52	10	4.55	5	3.04	20	4.64	20
4.27	25	4.18	55	2.65	25	4.53	15
4.12	5	4.02	15	2.50	5	4.11	20
3.92	10	3.87	10	2.28	10	4.04	25
3.83	15	3.75	10	2.23	10	3.97	20
3.75	5	3.52	15			3.74	20
3.52	10	3.42	10			3.60	5
3.40	5	3.34	5			3.45	5
3.34	15	3.28	10			3.18	10
3.23	15	3.22	15			3.07	100
3.16	60	3.13	100			2.83	10
3.10	30	3.08	50			2.73	5
2.95	10	2.93	10			2.70	15
2.77	5	2.78	20			2.63	20
2.74	20	2.68	30				
2.68	20	2.63	5				
2.54	10	2.54	10				

(*b*) K^+–Rb^+ *Ion-exchange Isotherms.*—Figure 1(*b*) shows the forward and reverse rubidium–potassium ion-exchange isotherms, which lie near the ideal curve having a unit gradient, thus showing, in terms of concentration, only a small preference for K^+. As with the K^+–Tl^+ isotherms, a narrow hysteresis loop occurred which in this case, holds in the range $\bar{x}_{\text{Rb}}$ *ca.* 0.20—0.55. The shapes of the ion-exchange isotherms in the other composition ranges strongly suggest that the Rb^+–K^+ processes take place *via* a solid–solution mechanism. *X*-Ray diffraction data in Figure 3 are in good agreement with this suggestion.

Figure 3(*a*) shows that for the $\text{K}^+ \longrightarrow \overline{\text{Rb}}^+$ process the lattice structure of the exchanger does not exhibit large variations until $\bar{x}_{\text{Rb}}$ 0.55. In the range $\bar{x}_{\text{Rb}}$ 0.55—0.45, the solid solution suddenly segregated so that only the $\overline{\text{Rb}_{0.9}\text{K}_{1.1}}$ (8.26 Å) phase was present at $\bar{x}_{\text{Rb}}$ 0.45. A further increase in the K^+ loading produced a $\overline{\text{KK}}$ (9.0 Å) phase while the amount of the $\overline{\text{Rb}_{0.9}\text{K}_{1.1}}$ (8.26 Å) phase decreased continuously to zero at $\bar{x}_{\text{Rb}}$ 0.14.

In the $\text{Rb}^+ \longrightarrow \overline{\text{K}}^+$ process, until $\bar{x}_{\text{Rb}}$ 0.24, the $\overline{\text{RbK}}$ phase was present as a very small percentage, because of the solubilisation of Rb^+ in the $\overline{\text{KK}}$ (9.0 Å) lattice. After this Rb^+ loading, *X*-ray diffraction patterns showed a remarkable increase in intensity of the 8.26 Å reflection to a maximum at $\bar{x}_{\text{Rb}}$ 0.41, thus suggesting the formation of an $\overline{\text{Rb}_{0.8}\text{K}_{1.2}}$ (8.26 Å) phase. A further increase in

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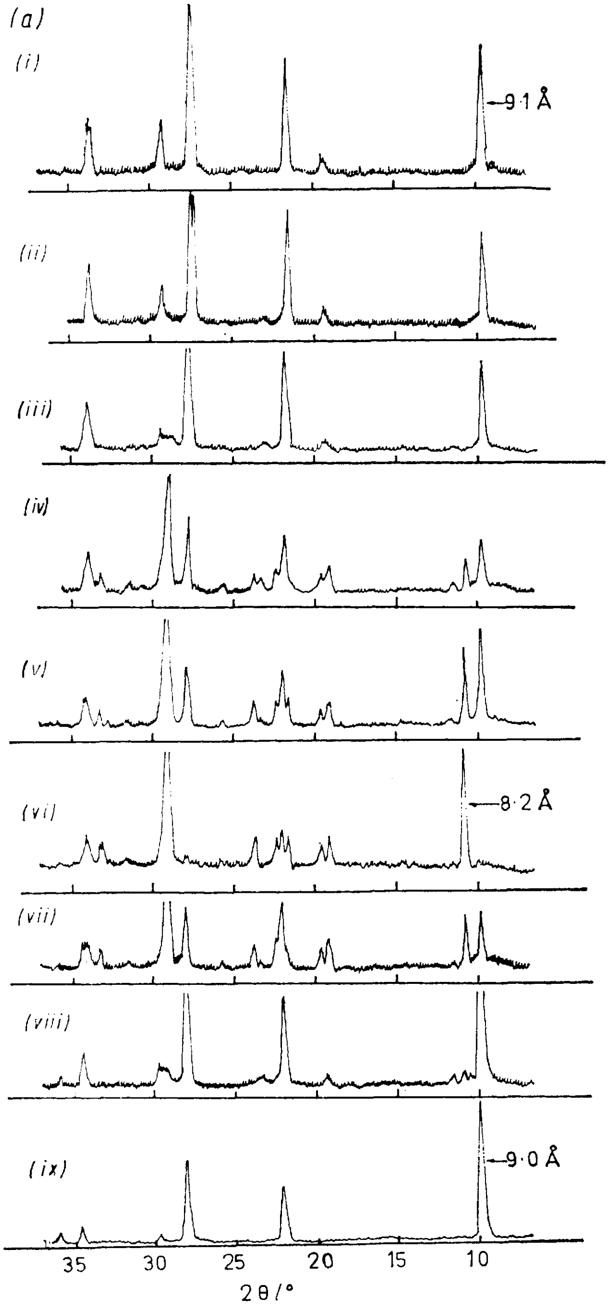
* For a rough estimate of the intensity values of the diffraction maxima, *X*-ray measurements were made on weighed samples having an equivalent amount of fixed groups.

[8] G. Alberti, S. Allulli, U. Costantino, and M. A. Massucci, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1779.

the Rb^+ loading produced a decrease in the amount of this phase which disappeared at $\bar{x}_{Rb}$ **0.58** in favour of a solid solution having an interlayer distance of **9.1** Å. The latter remained up to full conversion of the zirconium phosphate into the dirubidium form.

The overall Rb^+–K^+ ion-exchange processes can be summarised as in reaction (2). The formation of phases having different compositions in the forward and in the reverse process reasonably accounts for the presence of a narrow hysteresis loop in the ion-exchange isotherms.

The *d* values of the $\overline{Rb_{0.8}K_{1.2}}$ and $\overline{RbRb}$ phases are given in the Table. The $\overline{RbRb}$ phase has been previously characterized by dehydrating the hydrated form,[8] but its *d* values are given to show the good correspondence between the crystal structure of the two compounds.



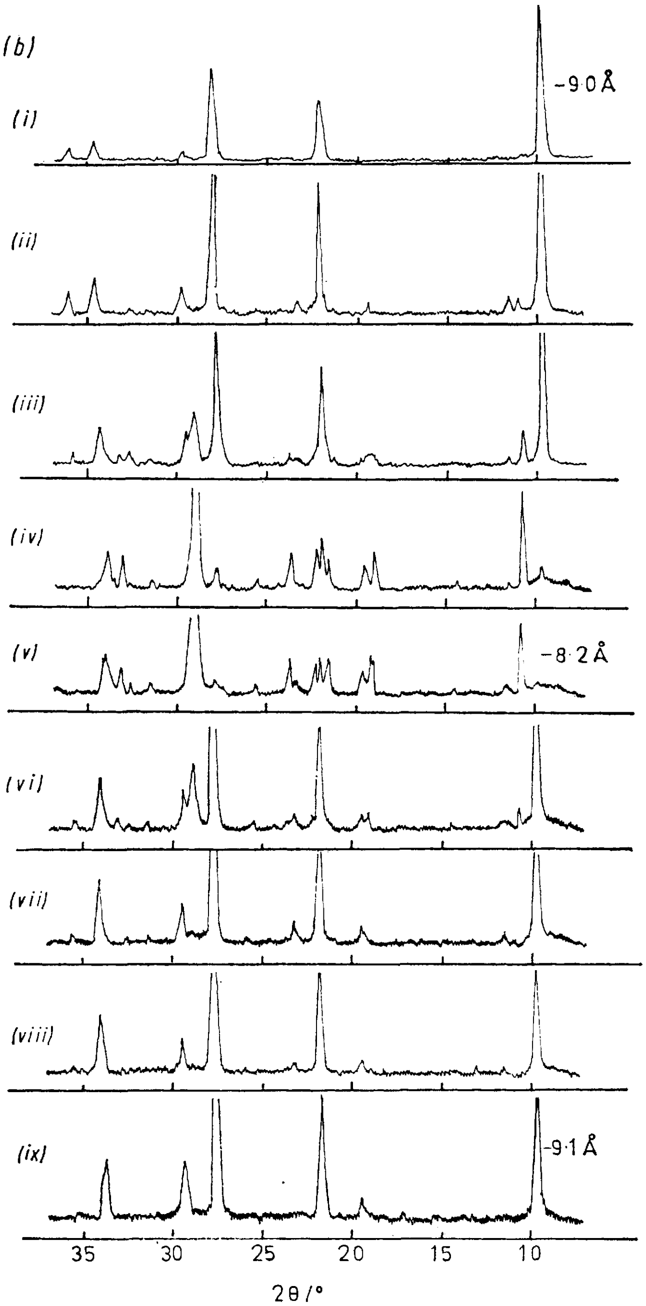
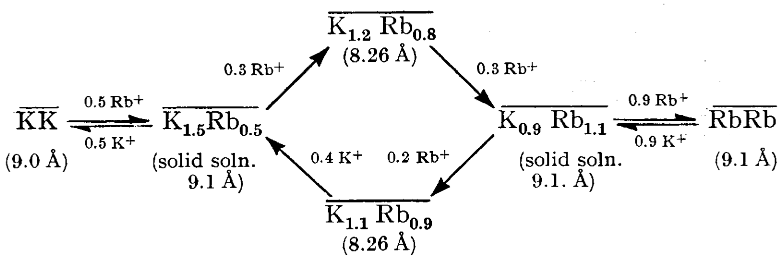


FIGURE 3 *X*-Ray diffraction patterns of several samples from the $Rb^+ \longrightarrow \overline{K^+}$ (*a*) and $K^+ \longrightarrow \overline{Rb^+}$ processes (*b*) in molten $K[NO_3]$–$Rb[NO_3]$ mixtures at 360 °C. Sensitivity, 2×10^3 counts s^{-1}. (*a*) $\bar{x}_{Rb} = 1.00$ (*i*), 0.89 (*ii*), 0.58 (*iii*), 0.46 (*iv*), 0.42 (*v*), 0.39 (*vi*), 0.36 (*vii*), 0.24 (*viii*), and 0.00 (*ix*); (*b*) $\bar{x}_{Rb} = 0.00$ (*i*), 0.14 (*ii*), 0.35 (*iii*), 0.40 (*iv*), 0.45 (*v*), 0.50 (*vi*), 0.55 (*vii*), 0.67 (*viii*), and 1.00 (*ix*)

(*c*) *Some General Considerations*.—A comparison between the K^+–Tl^+ and K^+–Rb^+ ion-exchange isotherms in Figure 1 reveals that the ion-exchange behaviour of Tl^+ and Rb^+ is very different.

These curves show that zirconium phosphate has a much larger preference for Tl^+ that for K^+, which, in turn, is slightly preferred when involved with Rb^+ in the ion-exchange experiments.



(2)

Taking into account that Rb^+ and Tl^+ have the same crystalline ionic radius, these findings must be ascribed to the difference in polarisability[9] of the two ions (α = 3.9 and 1.5 Å for Tl^+ and Rb^+).[3] The higher polarisability of Tl^+ allows both an easier steric accommodation of Tl^+ in the zirconium phosphate cavities and a higher electrostatic interaction energy with the fixed groups of the matrix. These considerations account well for the larger affinity of the exchanger for Tl^+ than Rb^+, and also for K^+ which has a smaller ionic radius (1.33 Å).

The shapes of the ion-exchange isotherms show reversible paths for a wide range of internal compositions, namely $\bar{x}_{Tl}$ 0—0.5 and 0.6—0.9, and $\bar{x}_{Rb}$ 0.55—1.0. These findings immediately suggest that the related equilibrium constants may be calculated to obtain a more quantitative assignment of the ion-exchange processes involved. A careful reconsideration of the equilibria (3)—(5) shows that only for (4) and (5) are there

$$\overline{KK} + Tl^+ \rightleftharpoons \overline{KTl} + K^+ \quad (3)$$

$$\overline{K_{0.8}Tl_{1.2}} + 0.6\,Tl^+ \rightleftharpoons \overline{K_{0.2}Tl_{1.8}} + 0.6K^+ \quad (4)$$

$$\overline{K_{0.9}Rb_{1.1}} + 0.9\,Rb^+ \rightleftharpoons \overline{RbRb} + 0.9K^+ \quad (5)$$

reversible ion-exchange processes without any simultaneous variation in the exchanger lattice.

In these cases, as well as for Li^+–K^+ and Li^+–Na^+ in fused nitrates,[2] we may adopt the formalism of Garfinkel[10] in calculating thermodynamic values for ion-

$$\log(x_{M'}/x_M)(A/2.303\,RT)(1 - 2x_M) = n\log(\bar{x}_{M'}/\bar{x}_M) - \log K \quad (6)$$

exchange processes between glass and molten salts [equation (6)]. Calculations made on this basis gave $K = 3.3$ and 0.24 for reactions (4) and (5), respectively, the values of the activities of the ions in the molten mixtures being obtained from refs. 11 and 12.

Both the K values agree well with the shapes of the ion-exchange isotherms, but mention must be made of the choice of the reference state which was based on all the cations exchangeable. This problem arises because crystalline zirconium phosphate is a polyfunctional exchanger, which means that several equilibrium constants in the process $\overline{MM} \longrightarrow \overline{M'M} \longrightarrow \overline{M'M'}$ must be considered.

Data of Alberti *et al.*[13,14] underline the strong influence of the cations present in the cavity in determining the ion-exchange behaviour of zirconium phosphate {*e.g.* Na^+–K^+ on $Zr[Na(PO_4)]_2{\cdot}3H_2O$ or $ZrHNa(PO_4)_2{\cdot}5H_2O$}. This implies that the cations which are not directly involved in the ion-exchange process can also give an entropic contribution to the equilibrium constant. Thus, the polyfunctionality of zirconium phosphate is related to the growth of various solid phases which, in turn, depend on the cations involved in the ion-exchange equilibrium. Therefore, we are critically evaluating other thermodynamic treatments[15] which take into account the activities of the phases.

Considering reaction (3), the situation is even more complicated since together with the ion-exchange reaction phase transitions occur, which prevent application of the above thermodynamic treatment. Recently, Clearfield and Medina[16] determined K_{eq} for the Na^+–H^+ processes on zirconium phosphate (which occur with phase transitions) by assuming that the initial and final phases both have unit activity. The equilibrium constants were calculated using the activities of the ions in solution. This clearly implies that the chemical potentials of the two phases present at the various equilibria do not influence one another. Our previous data on Li^+–Na^+ ion exchange on crystalline zirconium phosphate in molten nitrates[2] do not agree with this suggestion, and at the present the mechanism of the growth of a

[9] D. K. Sebera, 'Electronic Structure and Chemical Bonding,' Blaisdell, London, 1964.

[10] H. M. Garfinkel, *J. Phys. Chem.*, 1968, **72**, 4175.

[11] J. Lumsden, 'Thermodynamics of Molten Salt Mixtures,' Academic Press, New York, 1966.

[12] T. Forland in 'Fused Salts,' ed. B. R. Sundheim, McGraw-Hill, New York, 1964.

[13] G. Alberti, S. Allulli, U. Costantino, and M. A. Massucci, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1339.

[14] G. Alberti, U. Costantino, and J. P. Gupta, *J. Inorg. Nuclear Chem.*, 1974, **36**, 2103.

[15] F. Helfferich, 'Ion Exchange,' McGraw-Hill, New York, 1962.

[16] A. Clearfield and A. S. Medina, *J. Phys. Chem.*, 1971, **75**, 3750.

new crystalline phase during the exchange is under investigation.[17]

Thus, before calculating thermodynamic quantities for reaction (3), we think it is better to wait for an unambiguous definition of the model for ion-exchange processes occurring simultaneously with discontinuous phase rearrangement.

[6/221 *Received, 2nd February,* 1976]

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[17] S. Allulli and N. Tomassini, unpublished work.