Thermodynamic Treatment of Exchange of H^+ and K^+ in α-Titanium Phosphate

Carmen G. Guarido, Marta Suárez, José R. García, and Julio Rodríguez *
Departamento de Química Inorgánica, Facultad de Química, Universidad de Oviedo, C/Calvo Sotelo s/n, Oviedo, Spain

---

The H^+/K^+ ion-exchange process in α-titanium phosphate, $Ti(HPO_4)_2 \cdot H_2O$, was studied, titration curves and exchange isotherms being obtained at 25.0, 40.0, and 55.0 (±0.1) °C. Partial decomposition of the exchanger was detected. No partially substituted phases were detected by *X*-ray diffraction and the final product was $Ti(KPO_4)_2 \cdot 3H_2O$. The free energy, enthalpy, and entropy for the exchange reaction are determined, and the results are explained by means of structural considerations.

α-Titanium phosphate (α-TiP), $Ti(HPO_4)_2 \cdot H_2O$, has a lamellar structure with interconnected zeolitic cavities[1,2] which facilitates ionic diffusion in the solid and substitution of the hydrogen ions by other cations. Although the structure is not rigid (the distance between layers can be altered by entry into the zeolitic cavities of cations with large diameters), the higher the size of the cation retained by the material the greater is the activation energy. This fact can be clearly seen with alkali-metal ions because the substitution process only takes place in acidic media for Li^+ and Na^+,[2–10] it being necessary to provide the energy of the neutralization reaction in order for K^+ to be retained.[3,8,11]

In a previous paper[12] the existence of polyhydrated phases formed by total substitution by H^+/K^+ ion exchange in α-TiP was discussed. The failure to detect by *X*-ray diffraction the half-exchange phases was imputed to the low diffusion ability of K^+ in the exchanger structure which favoured the entry of a second cation into a lattice already deformed, instead of altering a new zeolitic cavity and disrupting the original cohesion forces. As a continuation of that study, the values of the thermodynamic functions for H^+/K^+ ion exchange in α-TiP were determined.

Experimental

Reagents.—All chemicals used were of reagent grade. The KOH solutions were standardized with HCl, which had previously been standardized with Na_2CO_3. The α-TiP was prepared as previously described.[12]

Analytical Procedures and Instrumental Techniques.—The pH measurements were made with a Crison model 501 pH-meter, equipped with glass and saturated calomel electrodes. The released phosphate groups were measured spectrophotometrically[13] with a Perkin-Elmer model 200 (λ = 315 nm). The K^+ in solution was determined by atomic absorption spectroscopy with a Perkin-Elmer model 372. The diffractometer used was a Philips model PV 1050/23 (λ = 1.5418 Å).

Ion-exchange Studies. The exchanger was equilibrated with 0.1 mol dm^{-3} (KOH + KCl) solutions at 25.0, 40.0, and 55.0 (±0.1) °C following the dynamic procedure of Clearfield *et al.*[14] The solid was present in the solution in a ratio of *ca.* 1 g : 500 cm^3. The equilibration time was 48 h.

Results and Discussion

Titration curves (Figure 1) at the three working temperatures showed good agreement, the pH varying almost linearly from 6.5 to 8.0. In the exchange isotherms (Figure 1) the amount of K^+ retained by the solid increased to a maximum value with increasing initial concentration of KOH, and then decreased. The maximum exchange values decreased as the temperature increased, as in the H^+/Na^+ exchange.[9]

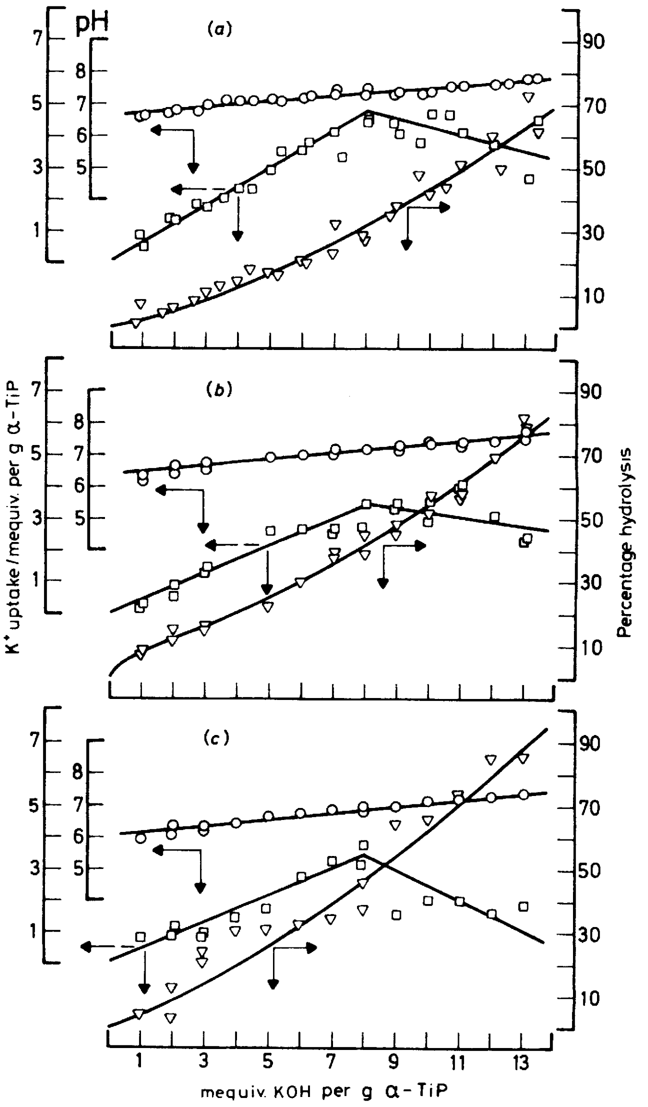

Figure 1. Titration curves (○), exchange isotherms (□), and hydrolysis of the exchanger (▽) at 25.0 (*a*), 40.0 (*b*), and 55.0 °C (*c*)

Partial decomposition of the exchanger was detected by measuring the phosphate groups present in solution (Figure 1).

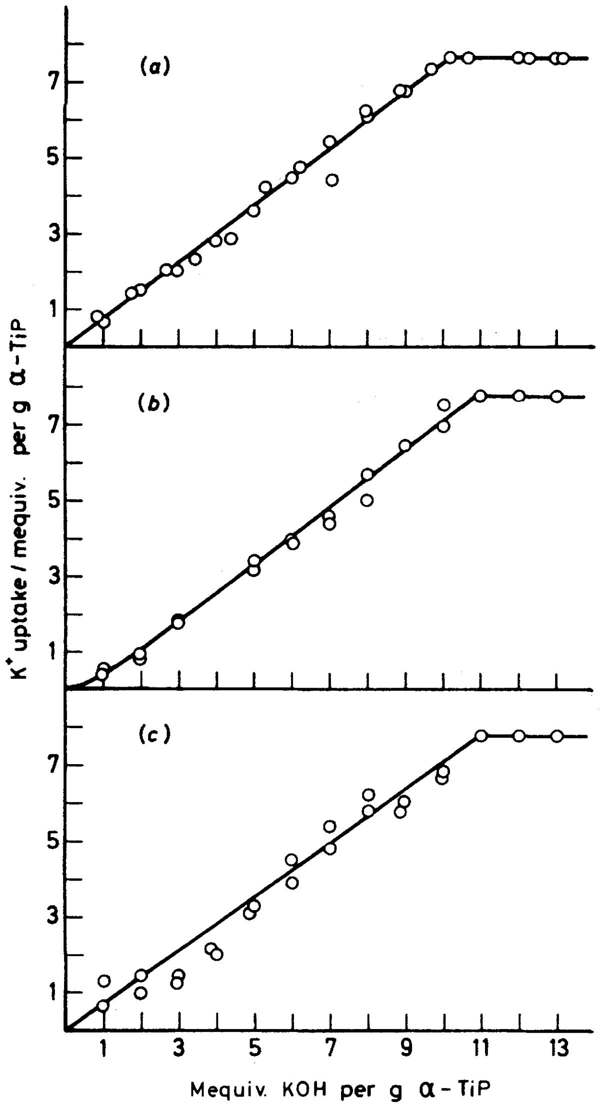

Figure 2. Exchange isotherms corrected for hydrolysis at 25.0 (*a*), 40.0 (*b*), and 55.0 °C (*c*)

The hydrolysis reactions, depending upon the equilibrium pH, were as in equations (1) and (2). Due to its larger size compared with Na^+ and Li^+, the diffusion of K^+ through the α-TiP layers was more difficult, the exchange process was slower, and the exchange remained longer in contact with alkaline solution. Therefore the extent of hydrolysis was greater. Taking into account the existence of hydrolysis, corrected exchange isotherms were obtained in which the extent of the exchange was referred to the amount of non-hydrolyzed α-TiP (Figure 2). As in earlier papers[6,9] it was assumed that the hydrolysis product ($TiO_2 \cdot nH_2O$) did not retain ions until α-TiP was totally saturated. When α-TiP was saturated, the exchange capacity was independent of the working temperature, corresponding to values of 0.2—0.5 equiv. K^+ per mol $TiO_2 \cdot nH_2O$ for equilibrium pH values between 7.3 and 8.4.

$$Ti(HPO_4)_2 \cdot H_2O + 4OH^- + (n-3)H_2O \longrightarrow TiO_2 \cdot nH_2O + 2HPO_4^{2-} \quad (1)$$

$$Ti(HPO_4)_2 \cdot H_2O + 2OH^- + (n-1)H_2O \longrightarrow TiO_2 \cdot nH_2O + 2H_2PO_4^- \quad (2)$$

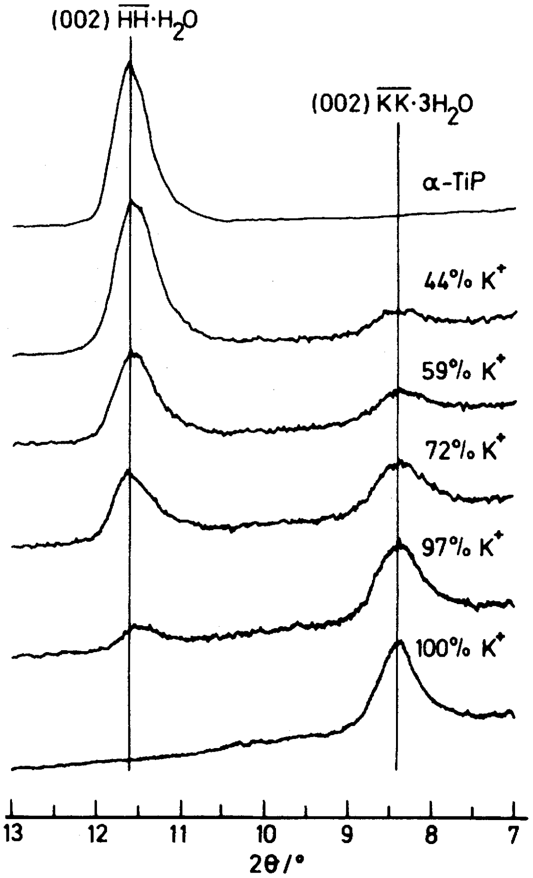

Figure 3. *X*-Ray patterns of some of the samples obtained at 25 °C and stabilized at a relative humidity of 100%

X-Ray patterns were similar at the three temperatures and qualitatively were the same as those previously reported at 5 °C.[12] Figure 3 shows the angular zone corresponding to the interlayer distance of samples obtained at 25 °C and stored in a relative humidity of 100%. Over the entire composition range, the coexistence of $Ti(HPO_4)_2 \cdot H_2O$ (7.6 Å) and $Ti(KPO_4)_2 \cdot 3H_2O$ (10.4 Å) phases was observed.

The exchange reactions on layered materials are usually irreversible[2] and so it is not possible to assign true thermodynamic values to them. Nevertheless, apparent thermodynamic data for the direct process of exchange can be obtained.[15] Eliminating the neutralization reaction, the H^+/K^+ substitution process took the form (3). According to the principle of microscopic reversibility,[16] the equilibrium constant is as in equation (4) where the quantities with bars represent species in the solid phase and those without the species in solution. In equivalent fraction terms this equation may be rewritten as in expression (5). For the solutions, we adopted the usual standard states which make the activities (*a*) of the ions equal to the corresponding molalities in solution at infinite dilution. The reference state of the solvent was also the one usually employed in which $a_w = 1$ for the pure solvent. The formation of a new crystalline phase coexisting with α-TiP suggested the existence in each phase of a unique class of counter ions and the constancy of the activity coefficient.[17] This made it possible to choose the standard state in which $a_H = a_K = 1$ and thus the equilibrium constant can be expressed as in equation (6). The concentrations of the species in the solid phase were expressed in terms of their respective molar fractions, while the concentrations of the species in solution were expressed in molalities corrected by the

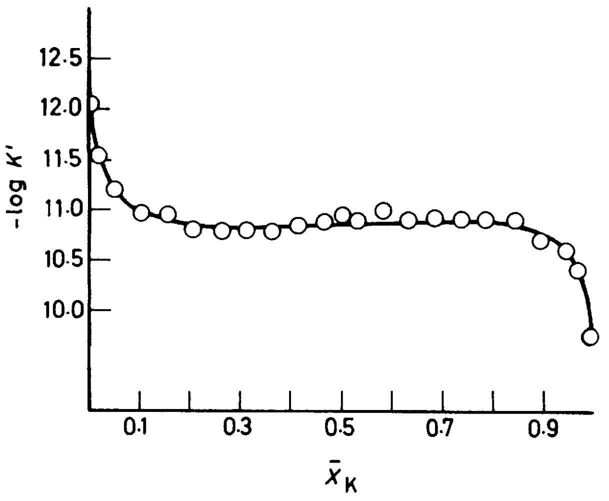

Figure 4. Plot of $-\log K'$ against $\bar{X}_K$ (25 °C)

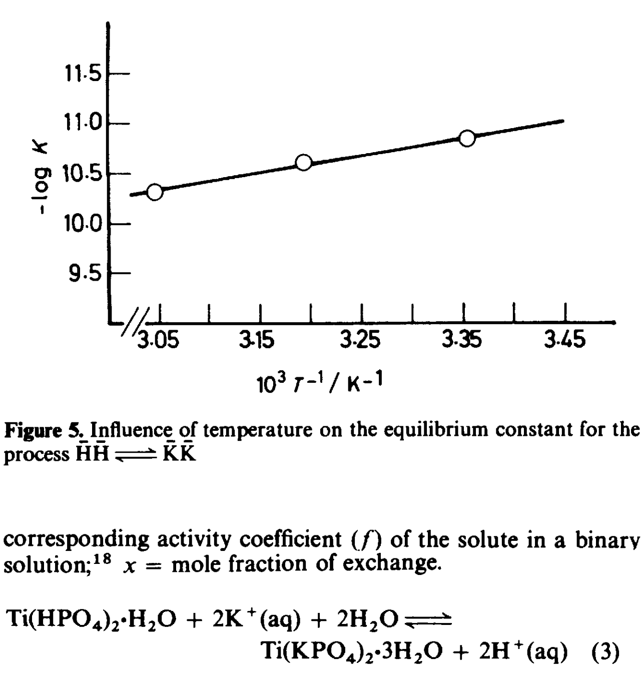

Figure 5. Influence of temperature on the equilibrium constant for the process $\bar{H}\bar{H} \rightleftharpoons \bar{K}\bar{K}$

corresponding activity coefficient (f) of the solute in a binary solution;[18] x = mole fraction of exchange.

$$\mathrm{Ti(HPO_4)_2{\cdot}H_2O} + 2\mathrm{K^+(aq)} + 2\mathrm{H_2O} \rightleftharpoons \mathrm{Ti(KPO_4)_2{\cdot}3H_2O} + 2\mathrm{H^+(aq)} \quad (3)$$

$$K = (\bar{a}_K a_H{}^2/\bar{a}_H a_K{}^2)(1/a_w{}^2) \quad (4)$$

$$K = (\bar{X}_K m_H{}^2/\bar{X}_H m_K{}^2)(\bar{f}_K f_H{}^2/\bar{f}_H f_K{}^2)(1/a_w{}^2) \quad (5)$$

$$K' = (\bar{X}_K m_H{}^2/\bar{X}_H m_K{}^2)(f_H{}^2/f_K{}^2) \quad (6)$$

The apparent equilibrium constant was obtained by application of the Gaines and Thomas thermodynamic treatment.[19] Since the exchanging ions are monovalent and the contribution of the water-activity term to log K is negligible, we obtain equation (7). The integral was calculated by plotting log K' against $\bar{X}_K$ and determining the area under the curve (Figure 4). Plotting the values of the equilibrium constant against $1/T$ (Figure 5) yielded ΔH°. The free energies were calculated from $\Delta G^\circ = -RT\ln K$ and the exchange entropies from $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. The following results were obtained: $\Delta H^\circ = 31.0$ kJ mol^{-1}, $\Delta G^\circ = 62.3$ kJ mol^{-1}, and $\Delta S^\circ = -105$ J K^{-1} mol^{-1}.

$$\log K = \int_0^1 \log K' \mathrm{d}\bar{X}_K \quad (7)$$

Studies of the thermodynamics of exchange of alkali-metal cations in α-ZrP,[15] isomorphic with α-TiP,[1,20] have shown that the transformations in half-exchanged phases result in negative enthalpic variations, while the evolution of these phases to saturation generally occurs with $\Delta H^\circ > 0$. The same is true for $\mathrm{H^+/Na^+}$ ion exchange on α-TiP.[9] In the system studied in this paper, the saturated phase was reached directly. The strong endothermicity of the process is explained by the necessary spreading of the layers to allow the insertion of $\mathrm{K^+}$ and by the repulsive electrostatic forces between two ions with the same sign sharing a zeolitic cavity of small dimensions.

The attainment of a fully-exchanged phase with hydration (n) higher than one explains the negative value of ΔS°, *i.e.* it is the result of the increase in order. The numerical value of ΔS° corresponds to a gain of two molecules of water, confirming the formation of $\mathrm{Ti(KPO_4)_2{\cdot}3H_2O}$.

References

1 A. Clearfield, G. H. Nancollas, and R. H. Blessing, 'Ion Exchange and Solvent Extraction,' vol. 5, eds. J. A. Marinsky and Y. Marcus, Marcel Dekker, New York, 1973.
2 'Inorganic Ion Exchange Materials', ed. A. Clearfield, CRC Press, Boca Raton, 1982.
3 G. Alberti, P. Cardini-Galli, U. Costantino, and E. Torracca, *J. Inorg. Nucl. Chem.*, 1967, **29**, 571.
4 K. Takaguchi and I. Tomita, *J. Chromatogr.*, 1976, **118**, 263.
5 J. R. García, M. Suárez, and J. Rodríguez, *Solvent Extr. Ion Exch.*, 1984, **2**, 275.
6 C. G. Guarido, M. Suárez, J. R. García, R. Llavona, and J. Rodríguez, *J. Chem. Thermodyn.*, 1985, **17**, 63.
7 A. Clearfield and T. N. Frianeza, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1925.
8 G. Alberti, U. Constantino, and M. Luciani, *Gazz. Chim. Ital.*, 1980, **110**, 61.
9 M. Suárez, J. R. García, and J. Rodríguez, *J. Phys. Chem.*, 1984, **88**, 159.
10 J. R. García, M. Suárez, and J. Rodríguez, *Solvent Extr. Ion Exch.*, 1984, **2**, 289.
11 E. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3114.
12 J. R. García, M. Suárez, R. Llavona, and J. Rodríguez, *J. Chem. Soc., Dalton Trans.*, 1984, 2605.
13 O. B. Michelsen, *Anal. Chem.*, 1957, **29**, 60.
14 A. Clearfield, A. Oskarsson, and C. Oskarsson, *Ion Exch. Membr.*, 1972, **1**, 91.
15 L. Kullberg and A. Clearfield, *J. Phys. Chem.*, 1981, **85**, 1585.
16 A. Clearfield and A. S. Medina, *J. Phys. Chem.*, 1971, **75**, 3750.
17 N. G. Chernorukov and T. V. Prokof'eva, *Zh. Fiz. Khim.*, 1977, **51**, 1361.
18 R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1959.
19 G. L. Gaines and H. C. Thomas, *J. Chem. Phys.*, 1953, **21**, 714.
20 A. I. Volkov, G. I. Novikov, and N. A. Ivkovich, *Khim. Tekhnol. (Minsk)*, 1976, **10**, 46.

Received 15*th October* 1984; *Paper* 4/1769