Lamellar Inorganic Ion Exchangers. Proton–Copper(II) Ion Exchange in γ-Titanium Bis(hydrogenphosphate)

Celia Alvarez, Ricardo Llavona, José R. García, Marta Suárez, and Julio Rodríguez*
Departamento de Química Inorgánica, Facultad de Química, Universidad de Oviedo, c/Calvo Sotelo s/n, Oviedo, Spain

The behaviour of γ-$Ti(HPO_4)_2 \cdot 2H_2O$ in the exchange of Cu^{2+} has been studied. Exchange isotherms and pH curves were obtained at 25.0, 40.0, and 55.0 (±0.1) °C. Half-exchanged phases $TiHCu_{0.5}(PO_4)_2 \cdot 2.5H_2O$ (interlayer distance 12.4 Å), $TiHCu_{0.5}(PO_4)_2 \cdot H_2O$ (10.7 Å), and $TiHCu_{0.5}(PO_4)_2$ (9.4 Å) were detected. The crystalline solid phases were examined by *X*-ray diffraction. The free energy, enthalpy, and entropy of the exchange reaction are reported.

The interpretation of ion-exchange properties in clay minerals is very difficult due to their complexity. α-Zirconium bis(hydrogenphosphate) monohydrate, $Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP),[1] resembles clay minerals[2] especially montmorillonite[3] but it is a much simpler system. Its structure is layered with interconnected zeolitic cavities which explain its ion-exchange properties.[4–9] α-Titanium bis(hydrogenphosphate) monohydrate (α-TiP)[10] is isomorphic with α-ZrP,[11,12] both having a basal spacing of 7.6 Å.

The γ varieties of these materials have interlayer distances greater than those of the α forms, 12.2 (γ-ZrP)[13] and 11.6 Å (γ-TiP),[14] and thus show more ready diffusion of ions with large diameters.[9,15–18] Their structure is not so far known, but they have monoclinic symmetry.[19,20] The dimensions of the unit cell of γ-TiP are a = 5.29, b = 6.44, c = 23.94 Å, and β = 103.9°.[20]

α-Zirconium bis(hydrogenphosphate) hardly retains first-row transition-metal ions.[21] In the case of Cu^{2+}, the use of acetate solutions leads to almost quantitative retention.[9] In addition to interest in the ion-exchange reactions, the copper forms of zirconium phosphates are important due to their use as catalysts.[22–26]

This paper reports the ion exchange of Cu^{2+} in γ-TiP with formation of half-exchanged phases. For the sake of brevity, the various ionic forms are simply indicated by their counter ions (under a bar) and water contents, while their interlayer distances are reported in parentheses.

Experimental

Reagents.—All chemicals used were of reagent grade. γ-Titanium bis(hydrogenphosphate) was obtained by using 16.5 mol dm^{-3} H_3PO_4 and a reflux time of 10 d as previously described.[27]

Analytical Procedures.—The concentrations of phosphorus and titanium in the solids were determined gravimetrically.[28] The pH measurements were made in a Crison model 501 pH-meter. The released phosphate groups were measured spectrophotometrically[29] using a Perkin-Elmer model 200 instrument. The Cu^{2+} in solution was determined iodometrically[28] and by differential pulse polarography using a Metron model E-506. Thermogravimetric analysis (t.g.a.) was performed by a Setaram model MTB 10—8, differential thermal analysis (d.t.a.) by a Setaram model MTB-M4 instrument. The diffractometer used was a Philips model PV 1050/23 (λ = 1.5418 Å, 2θ scan rate 0.125—2° min^{-1}, chart speed 2 cm min^{-1}).

Ion-exchange Studies.—The exchanger was equilibrated with 0.02 mol dm^{-3} ($CuSO_4$ + H_2SO_4) solutions at 25.0, 40.0, and 55.0 (±0.1) °C following the procedure described by Clearfield *et al.*[30] The solid was present in the solution in the ratio of *ca.* 1 g: 250 cm^3.

Results and Discussion

Exchange isotherms and pH curves are shown in Figure 1. The substitution progresses at the same time as the Cu^{2+} is added. The theoretical exchange capacity of γ-TiP, derived from its

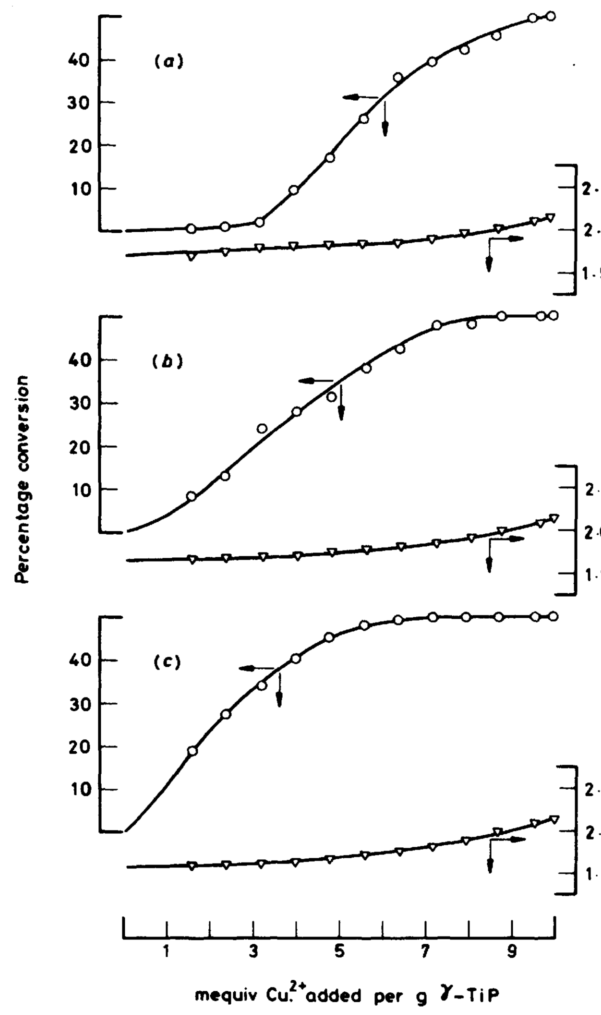

Figure 1. Exchange isotherms (○) and pH curves (▽) of γ-TiP at 25.0 (*a*), 40.0 (*b*) and 55.0 °C (*c*)

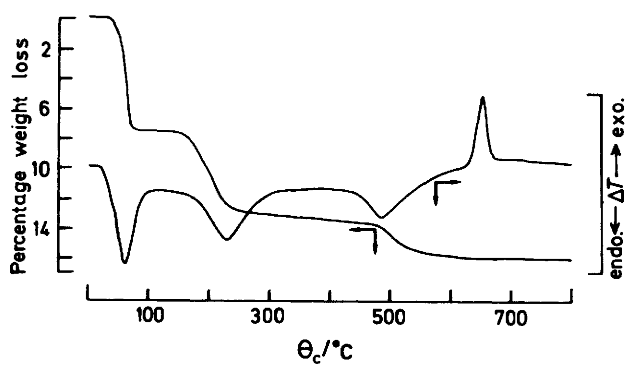

Figure 2. D.t.a. and t.g.a. curves of the half-exchanged phase stabilized in air

Table. *X*-Ray diffraction data for the half-exchanged phase stabilized in air, at 80, or at 200 °C

$\overline{HCu_{0.5}}\cdot 2.5H_2O$		$\overline{HCu_{0.5}}\cdot H_2O$		$\overline{HCu_{0.5}}$	
d/Å	I/I_0	*d*/Å	I/I_0	*d*/Å	I/I_0
12.4	35	10.7	10	9.4	30
6.14	45	6.03	10	5.28	15
5.09	5	5.40	8	4.47	20
4.36	20	5.02	5	3.97	10
3.99	8	4.75	5	3.65	5
3.55	100	4.53	15	3.46	100
3.15	50	3.72	100	3.18	70
2.93	20	3.15	30	3.03	15
2.69	5	2.92	10	2.53	8
2.56	20	2.70	5	2.46	5
2.51	10	2.53	10	2.36	5
2.37	5				

formula, $Ti(HPO_4)_2\cdot 2H_2O$, is 7.25 mequiv. per g. Conversions of 50% are reached more easily the higher is the temperature. The equilibrium pH slightly increases with the degree of conversion. The hydrolysis of the exchanger was $\leqslant 1\%$, as determined from the analysis of phosphorus in the equilibrium solutions. Treatment of the exchanged solids with hydrochloric acid solutions and subsequent analysis of phosphorus in solution indicate that there is no precipitation of copper phosphate.

Thermal analysis of the half-exchanged phase stabilized in air (Figure 2) shows the existence of three well differentiated zones of mass loss. The first occurs at 50—75 °C, the second at 150—250 °C, and the third of over 450 °C. These losses are in the ratio 3:2:1. The temperature zones in which they take place indicate that the two first processes are associated with the loss of water of crystallization and the third with condensation of the phosphate into pyrophosphate.[31,32] On the basis of the results obtained, the thermal behaviour of the half-exchanged phase at temperatures lower than that corresponding to condensation of the phosphate groups can be summarized as follows as in (1).

$$TiHCu_{0.5}(PO_4)_2\cdot 2.5H_2O \longrightarrow TiHCu_{0.5}(PO_4)_2\cdot H_2O \longrightarrow TiHCu_{0.5}(PO_4)_2 \quad (1)$$

X-Ray diffraction data of the exchange phase stabilized in air or treated at 80 or 200 °C are collected in the Table. The interlayer distance decreases with the degree of hydration.

When H^+ is replaced by another cation in lamellar exchangers of the α- or γ-zirconium phosphate type, the arrangement of the layers remains unaltered but the distance between them usually varies.[9,33–35] Kullberg and Clearfield[36] proposed to eliminate the contribution of the cation size by means of the use of a corrected interlayer distance which must be a direct function of the hydration degree of each crystalline phase [equation (2)], where Φ_M and $\Phi_{M'}$ are the counter ion

$$d_{corr.} = d - \frac{\Phi_M + \Phi_{M'}}{2} \quad (2)$$

diameters. Plotting this function against the water content of each phase gave straight lines for the substituted phases of α-ZrP,[36] α-TiP,[37] and γ-TiP.[38] A zone characteristic of the corrected interlayer distance for each water content is known in the case of γ-TiP (Figure 3). In order to calculate the corrected interlayer distance, the values of 0.35 (H^+) and 0.69 Å (Cu^{2+}) for the ionic radii are taken. The behaviour of the half-exchanged copper phases is in good agreement with the rest of the substitution phases of γ-TiP (Figure 3).

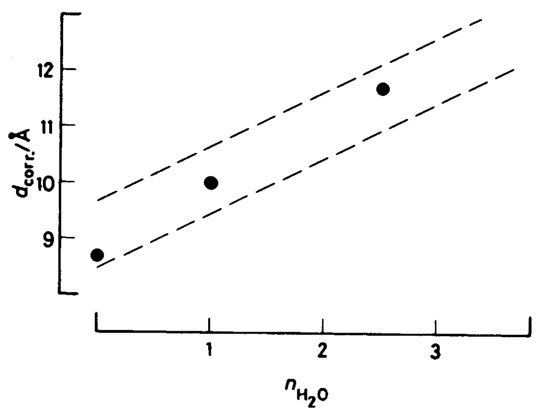

Figure 3. Corrected interlayer distance of the half-exchanged phase as a function of the water content. The dashed lines limit the zone of the corrected interlayer distance characteristic of the exchanged forms of γ-TiP[39]

X-Ray diffraction is an adequate technique for the study of lamellar ion exchangers. In Figure 4, *X*-ray patterns of samples with $0.00 \leqslant \bar{X} \leqslant 0.50$ composition are shown, where $\bar{X}$ is the molar fraction of exchange defined as the fraction of hydrogens substituted in γ-TiP; its value is the equivalent fraction of Cu in the solid when all the interchangeable hydrogens of the exchanger are involved in the substitution process. When the samples are stabilized in air [Figure 4(*a*)], two reflections in the zone of interlayer distance corresponding to the $\overline{HH}\cdot 2H_2O$ (11.6 Å) and $\overline{HCu_{0.5}}\cdot 2.5H_2O$ (12.4 Å) phases can be observed over the entire composition range. *X*-Ray patterns of samples of intermediate composition may be reproduced by combining those corresponding to the pure phases ($\overline{HH}\cdot 2H_2O$ and $\overline{HCu_{0.5}}\cdot 2.5H_2O$). This indicates the formation during ion exchange of an individual crystalline phase of composition $TiHCu_{0.5}(PO_4)_2\cdot 2.5H_2O$ coexisting with the initial one until $\bar{X} = 0.50$. When the samples are treated at 80 °C the *X*-ray patterns show [Figure 4 (*b*)] the coexistence of the $\overline{HH}$ (9.1 Å) and $\overline{HCu_{0.5}}\cdot H_2O$ (10.7 Å) phases.

X-Ray patterns of samples treated at 200 °C give less information about the ion-exchange process [Figure 4(*c*)]. The crystalline phases stable at this temperature have very similar interlayer distances, $\overline{HH}$ (9.1 Å) and $\overline{HCu_{0.5}}$ (9.4 Å), which tend to result in an unique reflection. γ-Titanium bis(hydrogenphosphate) and its exchanged phases have monoclinic symmetry,[20] the unit-cell parameters *a* and *b* being associated with the structure of the layers, *c* and β corresponding to the magnitude of the interlayer distance. Assuming that the entry of Cu^{2+} into

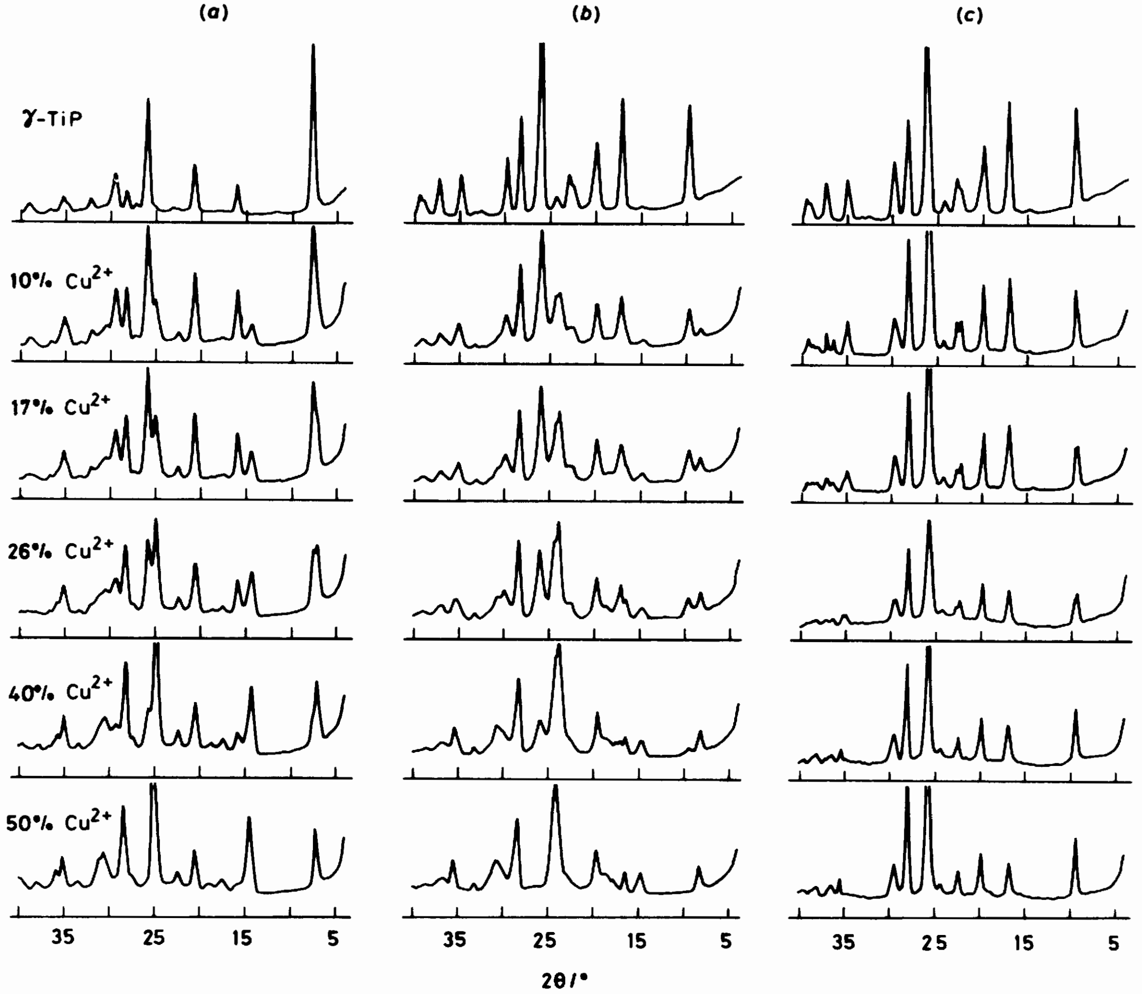

Figure 4. *X*-Ray patterns of some exchanged solids obtained at 25.0 °C, stabilized in air (*a*), at 80 °C (*b*), or at 200 °C (*c*)

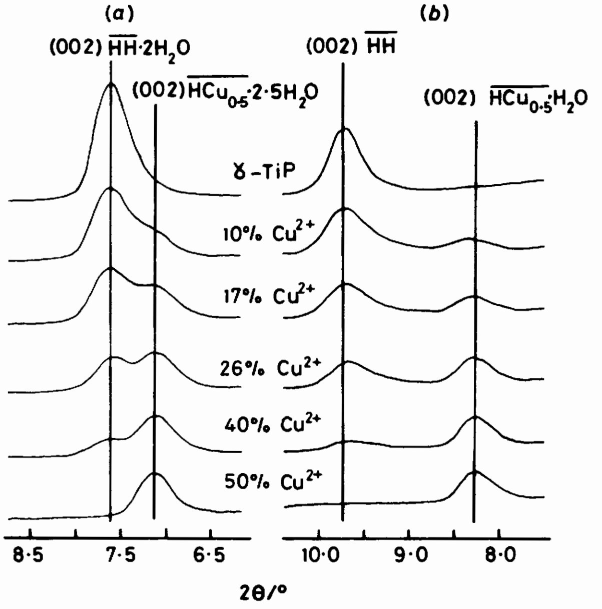

Figure 5. Detailed study by *X*-ray diffraction of the lines corresponding to the interlayer distance of the exchanged solids obtained at 25.0 °C stabilized in air (*a*) or at 80 °C (*b*)

the γ-TiP structure does not appreciably distort the structural arrangement of the layers, the *a* and *b* values should be the same in the exchanged phases. These values are not altered during the heat treatment. Moreover, if the interlayer distances of the phases are very similar, the values of *c* and β will be very similar, too. It is expected (and is demonstrated experimentally) that the two crystalline phases behave in a similar way towards *X*-rays.

When the solids are stabilized in air or treated at 80 °C, quantitative data can be obtained from *X*-ray diffraction by measuring the relative intensity of the reflections associated with the interlayer distances of the crystalline phases present in the sample (Figure 5).

The lamellar compounds are notorious for exhibiting preferred orientation, which affects the intensity measurements in *X*-ray diffraction.[39] Errors in intensity measurements are minimized by grinding the γ-TiP to a particle size smaller than 30 μm, by dividing each sample into five portions, and obtaining the average value of the corresponding five determinations. The variation of the relative intensity (determined by cutting out the peak areas and weighing them) of the phases present under the reported conditions is plotted in Figure 6.

In lamellar materials, the concentration (c_j) of a crystalline phase *j* in a mixture is a linear function of its relative intensity (I_j) [equation (3)],[40,41] where f_j is constant for each crystalline phase. The molar fraction of exchange will be given by equation (4). From this, equation (5) is deduced.

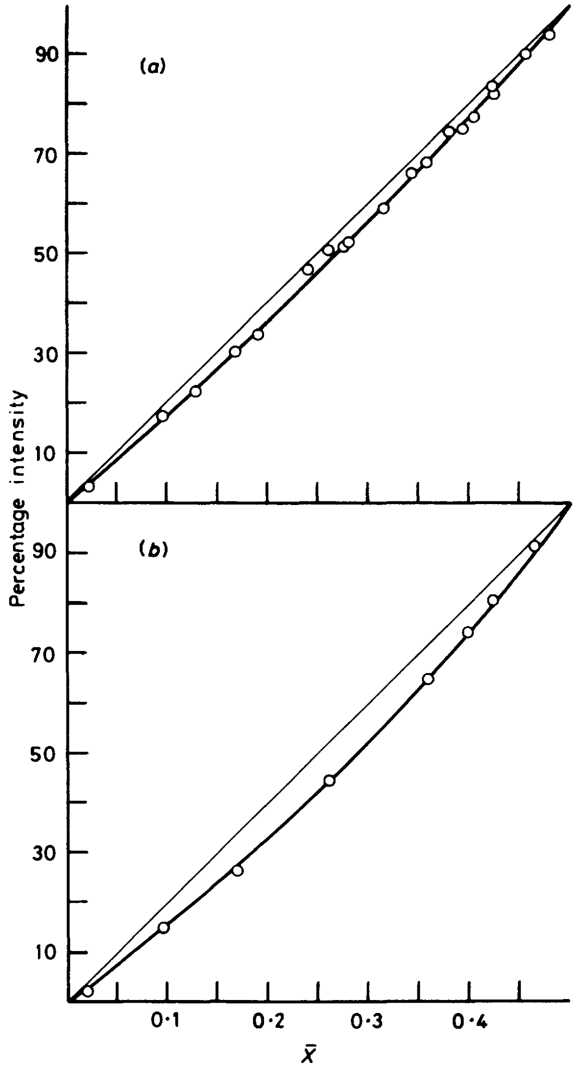

Figure 6. Variation of the intensity of the reflection corresponding to the interlayer distance of $\overline{HCu_{0.5}}\cdot 2.5H_2O$ (12.4 Å) relative to that of the $\overline{HH}\cdot 2H_2O$ phase (11.6 Å) (*a*) and that of $\overline{HCu_{0.5}}\cdot H_2O$ (10.7 Å) relative to $\overline{HH}$ (9.1 Å) (*b*)

$$c_j = f_j I_j \tag{3}$$

$$\bar{X} = \frac{1}{2}\,\frac{f_{HCu_{0.5}}\, I_{HCu_{0.5}}}{f_{H\bar{H}}\, I_{H\bar{H}} + f_{HCu_{0.5}}\, I_{HCu_{0.5}}} \tag{4}$$

$$\frac{f_{HCu_{0.5}}}{f_{H\bar{H}}} = \frac{2\bar{X}}{1 - 2\bar{X}} \cdot \frac{I_{H\bar{H}}}{I_{HCu_{0.5}}} \tag{5}$$

By application of expression (5) to the data collected in Figure 6, f_j is obtained under both measurement conditions: $f_{\overline{HCu_{0.5}}\cdot 2.5H_2O}/f_{\gamma\text{-}\overline{HH}} = 1.16$ and $f_{\overline{HCu_{0.5}}\cdot H_2O}/f_{\beta\text{-}HH} = 1.37$. These data allow the direct transformation of intensity into concentrations and give a rapid and accurate method for the control of the saturation degree of γ-TiP.

A systematic study of these ion-exchange materials requires thermodynamic data on the exchange reactions. The exchange reaction can be expressed in its ionic form as in equation (6). By making certain assumptions as in previous work,[16] thermodynamic data for the direct exchange process can be obtained. In agreement with the principle of microscopic reversibility,[42] the equilibrium constant takes the form of equation (7), where the

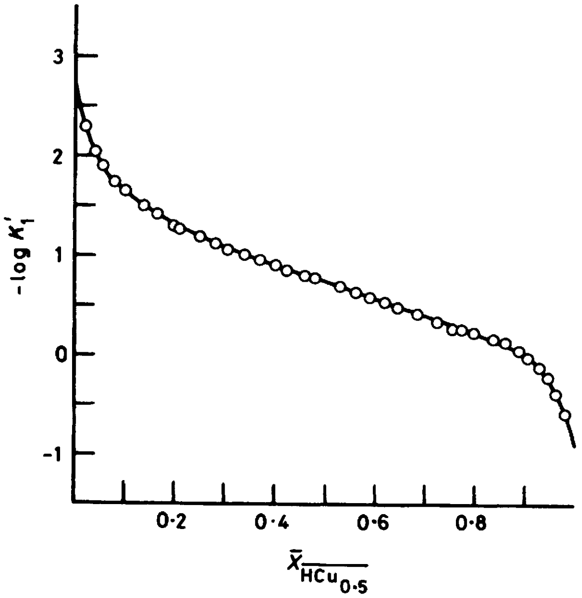

Figure 7. Plot of $-\log K_1'$ against $\bar{X}_{\overline{HCu_{0.5}}}$ (25.0 °C)

$$2\,H^+(c) + Cu^{2+}(aq) \rightleftharpoons Cu^{2+}(c) + 2\,H^+(aq) \tag{6}$$

$$K = (\bar{E}_{Cu} m_H{}^2/\bar{E}_H{}^2 m_{Cu})(\bar{f}_{Cu} f_H{}^2/\bar{f}_H{}^2 f_{Cu}) \tag{7}$$

quantities with bars represent the species in the solid phase while those without bars the species in solution. The concentrations of the species in the solid phase are expressed in terms of their respective equivalent fractions ($\bar{E}$), taking into account that the γ-TiP in this process has only 1 mol of interchangeable hydrogen ions per mol of exchanger so that its 'real' exchange capacity is 3.62 mequiv. per g. The concentrations of the species in the solution phase are expressed in terms of molalities corrected for the activity coefficient (f) in a binary solution.[43]

In solution, the usual standard state where the activities of the ions are equal to the corresponding molalities in solution at infinite dilution is taken. The reference state of the solvent is also as usual in that $a_w = 1$ for the pure solvent. For the solid phase we choose the reference state in which the solid is in equilibrium with an infinitely dilute solution of the counter ion, *i.e.* for $\bar{E}_H = 1$ and $a_w = 1$, $\bar{f}_H = 1$ and for $\bar{E}_{Cu} = 1$ and $a_w = 1$, $\bar{f}_{Cu} = 1$.

The equilibrium quotient expressed in equation (8) is evaluable over the entire composition range since we know the f ratio.[43] The equilibrium constant is obtained from equation (9) by applying the thermodynamic treatment of Gaines and Thomas,[44] where a and b are the water activities of solutions in equilibrium with pure forms of the exchanger, Z are the valences of the ions, and n_w refers to the number of water molecules of one 'exchange equivalent' of the solid. The second and fourth terms of equation (9) can be omitted without significant error,[45] yielding equation (10).

$$K' = (\bar{E}_{Cu} m_H{}^2/\bar{E}_H{}^2 m_{Cu})(f_H{}^2/f_{Cu}) \tag{8}$$

$$\ln K = (Z_H - Z_{Cu}) + \ln(\bar{f}_{Cu}/\bar{f}_H{}^2) + \int_0^1 \ln K'\, d\bar{E}_{Cu} - Z_H Z_{Cu} \int_a^b n_w\, d\ln a_w \quad (9)$$

$$\ln K = (Z_H - Z_{Cu}) + \int_0^1 \ln K'\, d\bar{E}_{Cu} \quad (10)$$

In order more clearly to express the ion-exchange process, the equilibrium reaction can be represented in terms of the solid phases involved as in reaction (11). This has the advantage of indicating the composition of the crystalline solid phases involved and, thus, the 'real' exchange capacity of the exchanger in the substitution step considered. From equation (11), we can define an equilibrium quotient in the form (12), which is related to K' as in (13). Equation (10) can be expressed, per mol of exchanger, in the form (14), where $K_1 = K^{\frac{1}{2}}$.

$$\mathrm{Ti(HPO_4)_2 \cdot 2H_2O\,(c)} + \tfrac{1}{2}\mathrm{Cu^{2+}(aq)} + (n-2)\,\mathrm{H_2O} \rightleftharpoons \mathrm{TiHCu_{0.5}(PO_4)_2 \cdot \mathit{n}H_2O\,(c)} + \mathrm{H^+(aq)} \quad (11)$$

$$K_1' = (\bar{E}_{Cu} m_H / \bar{E}_H m_{Cu}{}^{\frac{1}{2}})(f_H/f_{Cu}{}^{\frac{1}{2}}) \quad (12)$$

$$(K')^{\frac{1}{2}} = (\bar{E}_{Cu})^{-\frac{1}{2}} K_1' \quad (13)$$

$$\ln K_1 = -\tfrac{1}{2} - \tfrac{1}{2}\int_0^1 \bar{E}_{Cu} d\bar{E}_{Cu} + \int_0^1 \ln K_1'\, d\bar{E}_{Cu} = \int_0^1 \ln K_1'\, d\bar{E}_{Cu} \quad (14)$$

$$K_1' = (\bar{X}_{\overline{HCu_{0.5}}} m_H / \bar{X}_{\overline{HH}} m_{Cu}{}^{\frac{1}{2}})(f_H/f_{Cu}{}^{\frac{1}{2}}) \quad (15)$$

$$\log K_1 = \int_0^1 \log K_1'\, d\bar{X}_{\overline{HCu_{0.5}}} \quad (16)$$

The use of phase molar fractions is usual in studies of materials similar to γ-TiP, because it gives information about the system composition when several crystalline phases coexist.[40] For this reason, we replace the equivalent fractions of the ions in the solid phase ($\bar{E}$) by the corresponding phase molar fractions ($\bar{X}$). Since $\bar{E}_{Cu} = \bar{X}_{\overline{HCu_{0.5}}}$ and $\bar{E}_H = \bar{X}_{\overline{HH}}$ over the entire substitution range, the equilibrium quotient can be expressed as in equation (15) and, thus, the equilibrium constant can be calculated from expression (16). The integral is calculated by plotting $-\log K_1'$ against $\bar{X}_{\overline{HCu_{0.5}}}$ and determining the area under the curve (Figure 7). By plotting the equilibrium constants against $1/T$ (Figure 8) ΔH° is obtained. Using the equations $\Delta G^\circ = -RT\ln K$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ the following values are obtained: $\Delta H^\circ = 35.5$ kJ mol^{-1}, $\Delta G^\circ = 4.6$ kJ mol^{-1}, and $\Delta S^\circ = 104$ J K^{-1} mol^{-1}. Proton–copper(II) exchange in γ-TiP is a strongly endothermic process. At temperatures over 70 °C, ΔG° has a negative value and it might be expected that conversions of 50% would be more easily reached above this temperature.

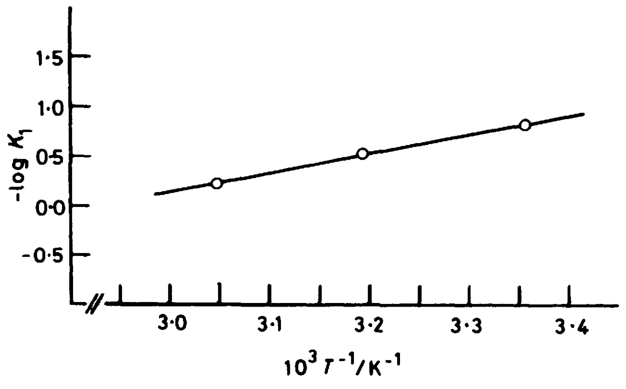

Figure 8. Influence of temperature on the equilibrium constant for $\overline{\mathrm{HH}} \cdot 2\mathrm{H_2O} \rightleftharpoons \overline{\mathrm{HCu_{0.5}}} \cdot n\mathrm{H_2O}$

Acknowledgements

This work was supported by the CAICYT (Project no. 84-0878) for which grateful acknowledgement is made.

References

1 A. Clearfield and J. A. Stynes, *J. Inorg. Nucl. Chem.*, 1964, **26**, 117.
2 D. Leigh and A. Dyer, *J. Inorg. Nucl. Chem.*, 1972, **34**, 369.
3 D. M. C. Macewan, 'The *X*-Ray Identification and Crystal Structure of Clay Minerals,' Mineralogical Society, London, 1961, ch. 4.
4 A. Clearfield and G. D. Smith, *Inorg. Chem.*, 1969, **8**, 431.
5 S. Ahrland and J. Albertsson, *Acta Chem. Scand.*, 1969, **23**, 1446.
6 S. E. Horsley, D. V. Nowell, and D. T. Stewart, *Spectrochim. Acta, Part A*, 1974, 30, 535.
7 J. M. Troup and A. Clearfield, *Inorg. Chem.*, 1977, **16**, 3311.
8 J. Albertsson, A. Oskarsson, R. Tellgren, and J. O. Thomas, *J. Phys. Chem.*, 1977, **81**, 1574.
9 'Inorganic Ion Exchange Materials,' ed. A. Clearfield, CRC Press, Boca Raton, Florida, 1982.
10 G. Alberti, P. Cardini-Galli, U. Costantino, and E. Torraca, *J. Inorg. Nucl. Chem.*, 1967, **29**, 571.
11 A. M. Landis and M. S. Thesis, Ohio University, Athens, 1970, p. 18.
12 'Ion Exchange and Solvent Extraction,' vol. 5, eds. J. A. Marinsky and Y. Marcus, Marcel Dekker, New York, 1973.
13 A. Clearfield, R. H. Blessing, and J. A. Stynes, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2249.
14 S. Allulli, C. Ferragina, A. La Ginestra, M. A. Massucci, and N. Tomassini, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1043.
15 M. Suárez, J. R. García, and J. Rodríguez, *J. Phys. Chem.*, 1984, **88**, 159.
16 C. G. Guarido, M. Suárez, J. R. García, and J. Rodríguez, *J. Chem. Soc., Dalton Trans.*, 1985, 1865.
17 R. Llavona, J. R. García, C. Alvarez, M. Suárez, and J. Rodríguez, *Solvent Extr. Ion Exch.*, 1986, **4**, 585.
18 R. Llavona, J. R. García, M. Suárez, and J. Rodríguez, *Thermochim. Acta*, 1986, **101**, 101.
19 S. Yamanaka and M. Tanaka, *J. Inorg. Nucl. Chem.*, 1979, **41**, 45.
20 E. Kobayashi and S. Yamazaki, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1632.
21 A. Clearfield and J. M. Kalnins, *J. Inorg. Nucl. Chem.*, 1976, **38**, 849.
22 A. Clearfield and S. P. Pack, *J. Catal.*, 1978, **51**, 431.
23 A. La Ginestra, C. Ferragina, M. A. Massucci, N. Tomassini, and A. G. Tomlinson, Proc. 5th Int. Conf. Therm. Anal., 1977, p. 424.
24 T. Hattori, H. Hanai, and Y. Murakami, *J. Catal.*, 1979, **56**, 295.
25 A. Clearfield, *J. Catal.*, 1979, **56**, 296.
26 A. Clearfield, D. S. Thakur, and H. C. Cheung, *J. Phys. Chem.*, 1982, **86**, 500.
27 R. Llavona, J. R. García, M. Suárez, and J. Rodríguez, *Thermochim. Acta*, 1985, **86**, 281.
28 I. M. Kolthoff, E. B. Sandell, E. J. Meehan, and S. Bruckenstein, 'Quantitative Chemical Analysis,' Nigar, Buenos Aires, 1972.
29 O. B. Michelsen, *Anal. Chem.*, 1957, **29**, 60.
30 A. Clearfield, A. Oskarsson, and C. Oskarsson, *Ion Exch. Membr.*, 1972, **1**, 91.
31 D. Dollimore, N. J. Manning, and D. V. Nowell, *Thermochim. Acta*, 1977, **19**, 37.
32 A. La Ginestra and M. A. Massucci, *Thermochim. Acta*, 1979, **32**, 241.
33 G. Alberti and U. Costantino, *J. Chromatogr.*, 1974, **102**, 5.
34 J. P. Gupta and D. V. Nowell, *Chem. Ind. (London)*, 1977, **15**, 649.
35 G. Alberti, *Acc. Chem. Res.*, 1978, **11**, 163.
36 L. H. Kullberg and A. Clearfield, *J. Phys. Chem.*, 1981, **85**, 1585.
37 J. R. García, M. Suárez, R. Llavona, and J. Rodríguez, *J. Chem. Soc., Dalton Trans.*, 1984, 2605.

38 R. Llavona, J. R. García, C. Alvarez, M. Suárez, and J. Rodríguez, *Solvent Extr. Ion Exch.*, 1986, **4**, 567.

39 H. P. Klug and L. E. Alexander, '*X*-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials,' Wiley, New York, 1974.

40 J. R. García, M. Suárez, C. G. Guarido, and J. Rodríguez, *Anal. Chem.*, 1984, **56**, 193.

41 R. Llavona, M. Suárez, J. R. García, and J. Rodríguez, *Anal. Chem.*, 1986, **58**, 547.

42 A. Clearfield and A. S. Medina, *J. Phys. Chem.*, 1971, **75**, 3750.

43 R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1959.

44 G. L. Gaines and H. C. Thomas, *J. Chem. Phys.*, 1953, **21**, 714.

45 R. M. Barrer and J. Klinowski, *J. Chem. Soc., Faraday Trans. 1*, 1974, 2080.

Received 15*th August* 1986; *Paper* 6/1671