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## Syntheses, Crystalline Structure, and Ion-Exchange Properties of Insoluble Acid Salts of Tetravalent Metals and Their Salt Forms

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Amorphous insoluble acid salts of tetravalent metals have been known for a long time, but starting from 1956 there has been increased interest in these compounds.<sup>1</sup> This revived interest is chiefly due to their good ion-exchange properties and their high resistance toward temperature and radiation, so that practical applications in nuclear technology or in ion-exchange processes occurring at high temperature were hoped for. Systematic studies were therefore performed in several laboratories. Almost all the possible combinations of tetravalent metals and polybasic acids were examined and the ion-exchange properties of the obtained precipitates investigated. Some of these materials exhibited the expected high stability toward radiation and temperature.<sup>2,3</sup> They are, however, not very stable toward hydrolysis of their acid groups, and therefore their composition is often not well defined.<sup>4-6</sup>

Starting from 1964 several insoluble acid salts of tetravalent metals were obtained as crystalline compounds,<sup>6-8</sup> and these materials were found to be considerably more stable than the amorphous ones.<sup>5,6,8</sup> Apart from their possible applications, the study of the insoluble acid salts of tetravalent metals is of interest in itself for the information that can be derived in several fields, such as the synthesis of new materials, the formation of crystalline precipitates, the sorption of ions by precipitates, electrical transport and self- or interdiffusion of counterions in crystals, structural chemistry, and phase transitions obtained by changing the counterions or the hydration water in the crystals, and so on.

Many interesting properties of the insoluble acid salts of tetravalent metals depend on the crystalline structure of the material obtained rather than on the metal ion or polyvalent acid involved. It is therefore convenient to discuss these materials according to their crystalline structure.

### Amorphous Acid Salts of Tetravalent Metals

These are usually obtained by direct mixing of a salt solution of a given tetravalent metal with an excess of

a polybasic acid. The protons of the acid groups of the insoluble acid salt can be replaced by other cations; therefore several acid salts possess an appreciable ion-exchange capacity. Furthermore, it was found that they have high selectivity for certain cations<sup>9-12</sup> and that this selectivity can be increased by thermal treatment.<sup>13-15</sup>

The systematic researches, essentially performed in view of their practical applications as inorganic ion exchangers, led also to a better understanding of their formation and composition. For example, it was found that the precipitate obtained by mixing a Zr(IV) salt solution and phosphoric acid, commonly reported in the literature as zirconyl phosphate, is a polyhydrated zirconium (bis monohydrogen orthophosphate), Zr-(HPO<sub>4</sub>)<sub>2</sub>·nH<sub>2</sub>O.<sup>4,7</sup> The interested reader is referred to ref 1, 2, 5, 6, and 16 for particulars on the synthesis and properties of amorphous materials.

### Crystalline Acid Salts of Tetravalent Metals

**Acid Salts with Layered Structure.** Some important insoluble acid salts of tetravalent metals with a layered structure are shown in Table I (see ref 6, 8, 17-26). Among them, the most investigated acid salt

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Table I  
Insoluble Acid Salts of Tetravalent Metals with a Layered Structure

Compound	Formula	Ion exchange capacity, mequiv/g	Density, g/cm <sup>3</sup>	Interlayer distance, Å	Ref
Titanium phosphate	Ti(HPO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	7.76	2.61	7.56	17, 18
Zirconium phosphate	Zr(HPO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	6.64	2.72	7.56	6, 8, 18
Hafnium phosphate	Hf(HPO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	4.17		7.56	19
Germanium(IV) phosphate	Ge(HPO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	7.08		7.6	20
Tin(IV) phosphate	Sn(HPO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	6.08	3.12	7.76	21, 22
Lead(IV) phosphate	Pb(HPO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	4.79		7.8	20
Titanium arsenate	Ti(HAsO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	5.78	3.34	7.77	26
Zirconium arsenate	Zr(HAsO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	5.14	3.39	7.82	23-25
Tin(IV) arsenate	Sn(HAsO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	4.80	3.75	7.77	22

is certainly the zirconium phosphate; therefore in this Account we shall consider in detail only this compound.

**Preparation of Zirconium Phosphate.** Zirconium phosphate is readily obtained by mixing an excess of phosphoric acid with aqueous solution of a zirconyl salt. Precipitation is very fast and leads to amorphous materials; however, crystalline materials can be obtained by slowing down considerably the rate of their precipitation. A suitable method, employed by Alberti and Torracca<sup>27</sup> to reduce this rate, is the following: zirconium is first complexed by adding an appropriate amount of hydrofluoric acid to the zirconyl salts, then the zirconium fluoro complexes are slowly decomposed in the presence of phosphoric acid (e.g., by removing the HF from the solution with a stream of nitrogen or water vapor). In such a manner, the rate of precipitation of the zirconium phosphate is controlled by the rate of removal of HF; if this rate is very slow, materials with a very high degree of crystallinity are obtained.

Alternatively, crystalline zirconium phosphate can be obtained, according to the Clearfield method,<sup>7</sup> by refluxing the amorphous product in concentrated phosphoric acid. In this case the degree of crystallinity of the materials depends on the refluxing time and on the concentration of the phosphoric acid. The formula of the crystalline zirconium phosphate in the hydrogen form is Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. Its density is 2.72 g/cm<sup>3</sup> and its ion-exchange capacity 6.64 mequiv/g.

**Crystalline Structure of Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O.** Before discussing the properties of the layered ion exchangers it is very useful to examine the crystal structure of zirconium phosphate, as worked out by Clearfield and Smith.<sup>6,18</sup> Each layer consists of zirconium atoms lying in a plane and bridged through phosphate groups located alternatively above and below this plane (Figure 1). Three oxygen atoms of each tetrahedral phosphate group are bonded to three zirconium atoms in the plane, so that an octahedral coordination of oxygen atoms around each zirconium atom is obtained.<sup>6,18</sup> The fourth oxygen atom of the phosphate group bears the fixed negative charge, neutralized by H<sup>+</sup> counterions. Each

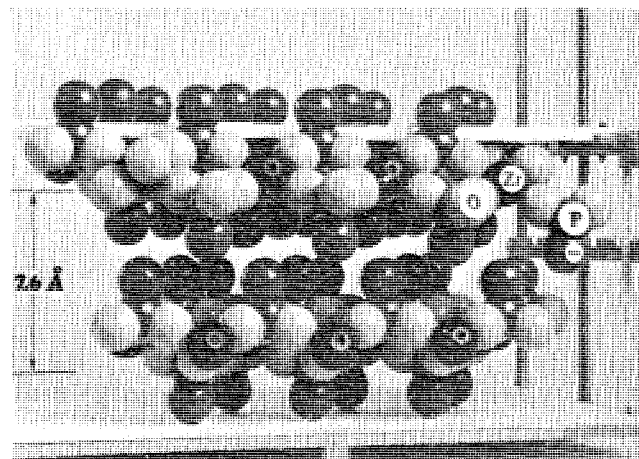


Figure 1. Idealized structure of two adjacent layers of zirconium phosphate in Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. (Interlayer distance 7.6 Å; protons and water are not shown in figure.)

layer can thus be considered as a polyvalent macroanion, Zr<sub>n</sub>(PO<sub>4</sub>)<sub>2n</sub><sup>2n-</sup>. The crystal structure of zirconium phosphate is built up by packing together these layers. The forces holding the layers are long hydrogen bonds and van der Waals forces. When the protons are replaced by other counterions, the forces are essentially ionic bonds between the negative fixed charges of two adjacent layers and the counterions placed between them.

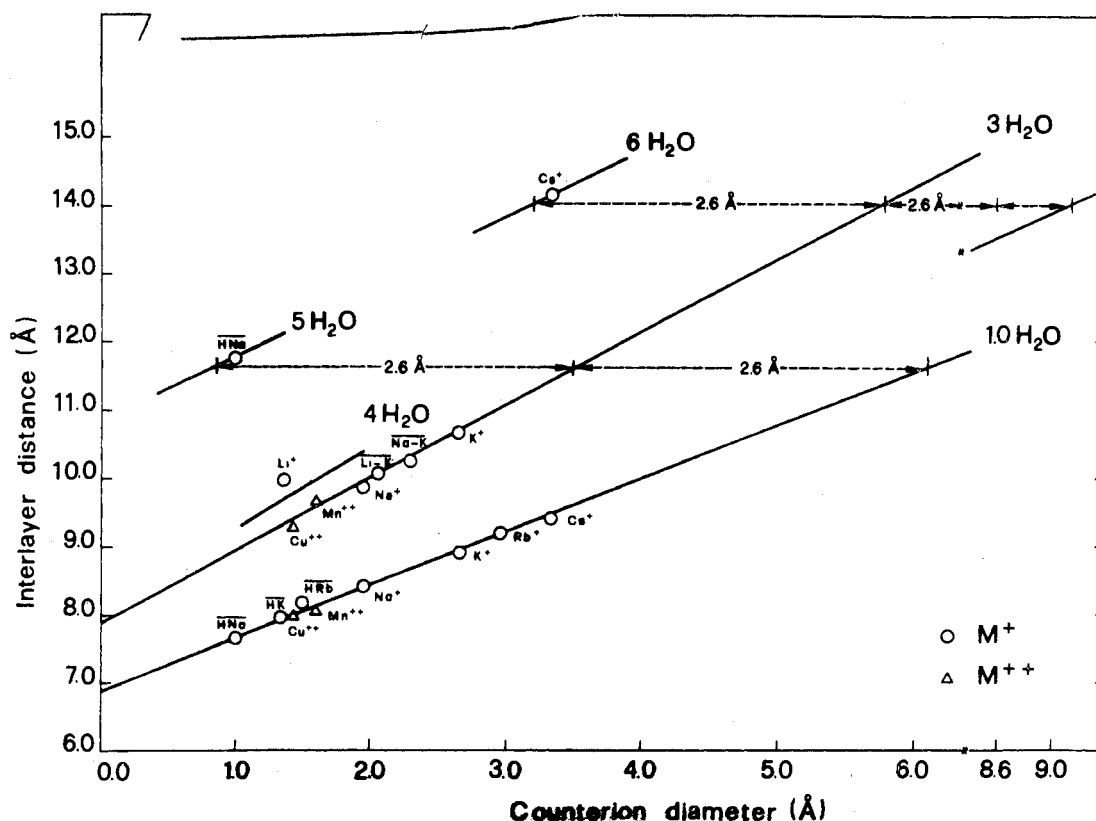
**Steric Hindrance to the Diffusion of Counterions.** In Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O each phosphorus atom in the lower layer lies along a perpendicular line drawn from the zirconium atom of the upper layer. This packing of the layers creates zeolitic-type cavities that are interconnected by openings<sup>6,28</sup> whose maximum size is 2.64 Å. Hence, counterions having a diameter greater than the latter value could not be taken up by Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O, because of steric hindrance. However, if sufficient energy for the exchange is supplied, i.e., by increasing the pH value of the external solution, the layers can spread apart and large cations such as Rb<sup>+</sup> or Cs<sup>+</sup> can enter inside the crystals.<sup>29</sup>

Taking into account the fact that several cations give insoluble hydroxides in alkaline medium, crystalline Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O can be employed only for a limited number of cations such as alkali metal ions, Ca<sup>2+</sup> and Sr<sup>2+</sup>. For this reason crystalline zirconium phosphate was regarded, until recently, as a poor exchanger, and although it is more stable than the amorphous product,

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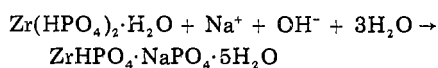
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**Figure 2.** Interlayer distance against the diameter (or average diameter) of the counterions for some mono-, tri-, penta-, and hexahydrated ionic forms of zirconium phosphate.

the latter is preferred for practical applications.

New possibilities for crystalline zirconium phosphate have been recently opened up by using ionic forms with large interlayer distance.<sup>30</sup> In fact, in contrast to zeolites, the windows connecting the cavities can be enlarged by replacing the protons with other counterions. Thus, by replacing one proton by  $\text{Na}^+$ , the monosodium form is obtained:



Concomitantly the interlayer distance increases from 7.6 to 11.8 Å. If  $\text{Na}^+$  is replaced by  $\text{H}^+$  (under suitable conditions), the monohydrated dihydrogen form is no longer formed, but a polyhydrated form, having 5–7 water molecules, is obtained.<sup>31,32</sup> The interlayer distance in this polyhydrated form is 10.4 Å.

It is evident from Figure 1 that by enlarging the interlayer distance the windows interconnecting zeolitic cavities are also enlarged. Steric impediments thus become progressively smaller, and the concept of zeolitic cavities for materials having large interlayer distance is lost. Indeed, we have found that the protons of the polyhydrated dihydrogen zirconium phosphate, or the  $\text{Na}^+$  ion of the monosodium form, can be easily replaced by large monovalent cations or hydrated polyvalent cations.<sup>33</sup> This makes it possible to obtain a large

number of different ionic forms. To date about 120 different ionic forms of zirconium phosphate have been prepared and their water content and interlayer distance determined. Interlayer distances of several ionic forms have already been reported in ref 8.

**Interlayer Distance of Zirconium Phosphate as a Function of Counterion Size and Water Content.** Since the reticular positions of the water and counterions are not yet known, it is of interest to obtain some preliminary information by studying the variation of the interlayer distance with counterion size and water content. As a rule, the interlayer distance increases with the water content and size of the counterion.

Figure 2 shows the interlayer distances against the diameter of the counterions for some hydrated salt forms. For the monohydrated forms, a straight line, with a slope of 0.80 and an intercept at 6.80 Å, has been obtained. It was also found that the interlayer distance of salt forms containing two different counterions M and M' approximately fit the same straight line if an average diameter  $(M + M')/2$  is used (for the  $\text{HM} \cdot \text{H}_2\text{O}$  salt forms the diameter of the proton is assumed to be negligible relative to that of M). It can be also observed that for  $\text{K}^+$  or larger counterions the interlayer distance is not appreciably decreased when the water molecule is lost. This fact suggests that the water molecule lies near the center of the cavity while each of the two counterions is placed between two fixed charges of two adjacent layers. The slight decrease in the interlayer distance obtained when the water molecule is lost by salt forms containing counterions smaller than  $\text{K}^+$  can be explained by assuming that the small counterions can slightly shift toward the center of the cavity as the water molecule is removed. It is interesting to note that a straight line is obtained also for the trihydrated forms.

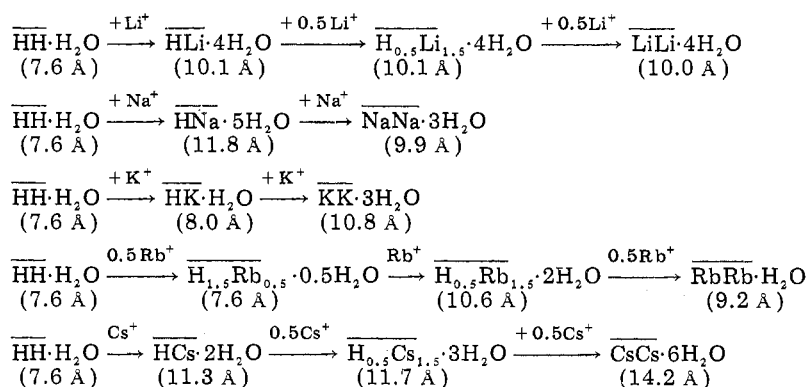
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## Scheme I



Furthermore, the difference between the interlayer distance of trihydrated and monohydrated forms is about 2.6 Å. Since this value is very near to the diameter of the water molecule, we think that in the trihydrated forms two water molecules (one for each counterion) lie along lines crossing the counterions and almost perpendicular to the layers while the third molecule is placed near the center of the cavity and does not contribute to the interlayer distance.

It can also be noted that the interlayer distance again increases by about 2.6 Å from trihydrated to pentahydrated forms. It is therefore very likely that for every two additional water molecules (one for each counterion) one monolayer of water is intercalated between the sheets. Thus, for an odd number of water molecules, the interlayer distance can be calculated from the simple formula:

interlayer distance (Å) =

$$6.80 + \left[ \frac{M + M'}{2} + \left( \frac{(n_{\text{H}_2\text{O}} - 1)}{2} \right) 2.6 \right] 0.80$$

The addition of one molecule of water to an odd-hydrated form does not appreciably increase the interlayer distance. Thus, we suggest that this water molecule is added around the cavity, and it influences the interlayer distance insofar as it increases the perpendicularity to the layers of the remaining water molecules. Thus, for an even number of water molecules, the interlayer distance can be calculated by subtracting 2 from  $n_{\text{H}_2\text{O}}$  and by increasing the value of the coefficient from 0.80 to 0.84.

**Ion-Exchange Mechanism of Zirconium Phosphate.** The knowledge of the structure of zirconium phosphate, the dependence of its interlayer distance on the size of the counterions involved and on the water content, as well as the shape of the ion exchange isotherm or the shape of the titration curves and the possibility of following, by x-ray diffraction, the phase transition from a stable interlayer distance to another during an ion-exchange process now make it possible to draw some general conclusions on the ion-exchange mechanism of the layered exchangers.

Let us first consider the phase transition during the exchange. X-ray analyses show that in many processes the change of the interlayer distance is discontinuous. A first important consequence of the phase transition is that two coexisting solid phases are present during each ion-exchange step; therefore the degree of freedom of the system (at constant temperature and pressure) is zero, and the ion exchange must occur at constant

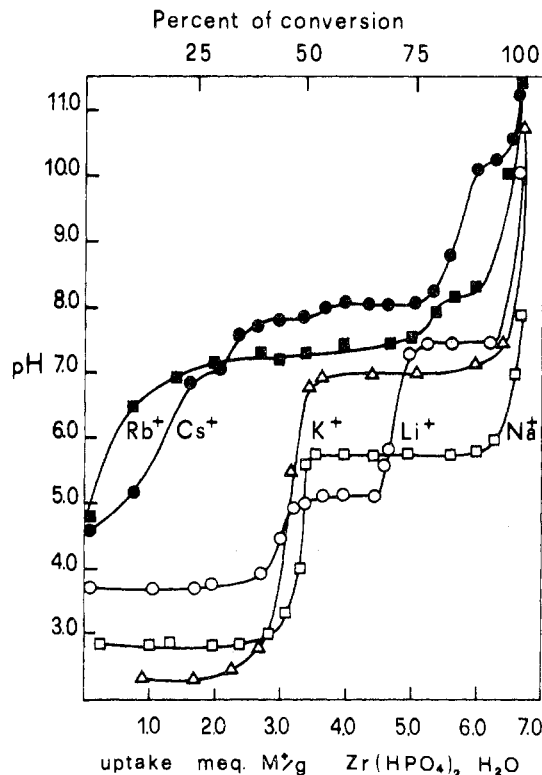


Figure 3. Uptake curves obtained by titrating  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  with alkali metal ion hydroxides in the presence of added 0.1 M salt. Conditions: 1 g of  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  in 200 mL of 0.1 N (MCl + MOH) solution at  $25 \pm 1^\circ \text{C}$ .

composition of the solution. Vertical portions in the ion-exchange isotherm (or plateau in the uptake curves) have indeed been found in many processes.<sup>6-8,34-40</sup> In Figure 3 are shown the uptake curves obtained with alkali metal ion hydroxides. The ion-exchange steps and the relative interlayer distances of the phases are given by Scheme I. It would take too long to discuss even briefly the numerous ion-exchange processes with

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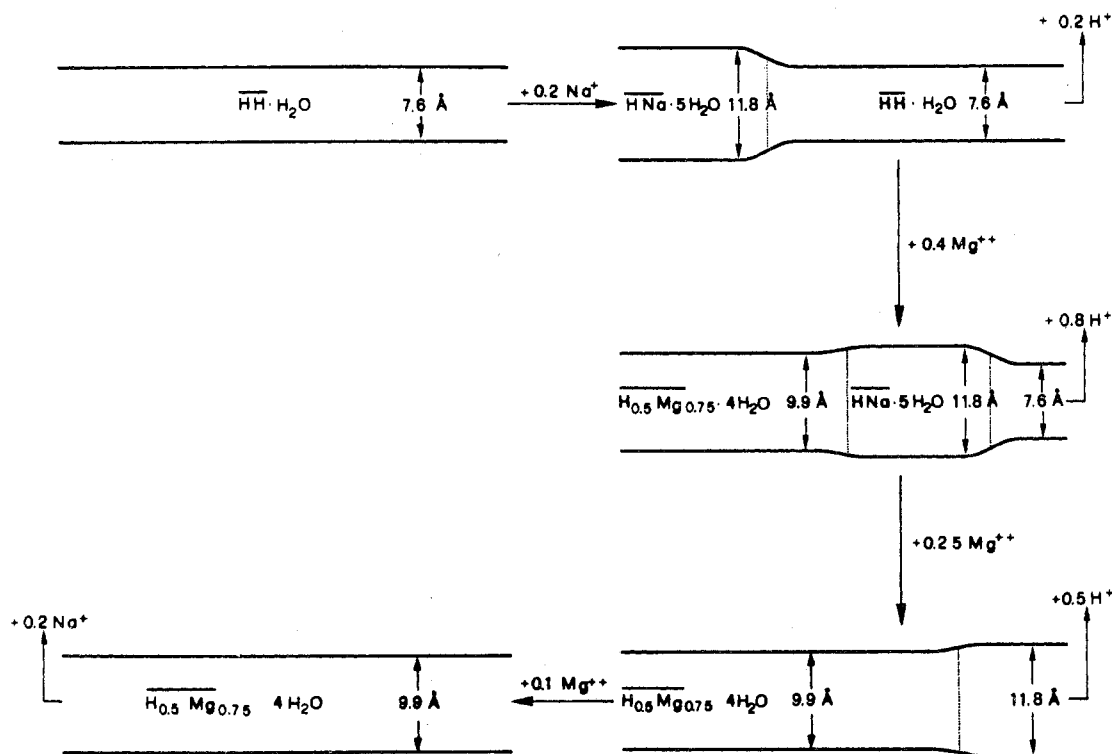
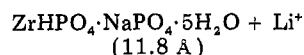
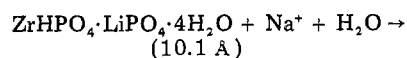


Figure 4. Catalytic effect of  $\text{Na}^+$  on the  $\text{Mg}^{2+}$  exchange on  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  according to the model of different coexisting solid phases in a single crystal of zirconium phosphate (schematic).

phase transition examined to date. As an example, we choose the single process



Since the process is discontinuous, when  $\text{Li}^+$  is partially replaced by  $\text{Na}^+$ , X-ray patterns show the presence of both 10.1 and 11.8 Å interlayer distances.<sup>30</sup> With increasing  $\text{Na}^+$  conversion, the intensity of the 10.1-Å peak decreases while that of the 11.8-Å peak increases. The problem that now arises is: when we have two coexisting phases with differing interlayer distances, are they present in different crystallites or in a single crystal? Since in a single layer of zirconium phosphate each zirconium atom is covalently bonded to six oxygens of six different phosphate groups, it is unlikely that the structure of the layer is broken during a phase transition; thus, in our opinion, the layers are not broken, but only bent in order to join together the parts of the crystal with a different interlayer distance.

Preliminary attempts to see directly the two coexisting phases in a single crystal under an optical microscope have been unsuccessful owing to the small size of the crystals. However, this coexistence is already known to occur in some natural large crystals with layered structure, such as vermiculite;<sup>41</sup> furthermore, dehydration studies of partially converted phases seem to indicate the presence of two phases in a single particle.<sup>42</sup> The model of different coexisting interlayer distances in a single crystal leads to some interesting implications, and it can be used to explain, in a simple manner, various ion-exchange processes occurring in a layered exchanger. Taking into account that in an

ion-exchange process the replacement of the counterions starts in the external part of the crystal in contact with the equilibrating external solution, it may be expected that the new phase also starts to be formed in the external part of the crystal and that the phase boundary always moves from the external toward the central part of the crystal. Thus, the reciprocal position of the two coexisting phases in the forward and reverse processes should be inverted. As a consequence, taking into account that the ion exchange occurs at the phase boundary and that the counterions involved must cross the external part of the crystal, it is expected that the rate of the ion exchange depends on whether the interlayer distance of the external part is larger or smaller than the internal one.

Let us show how the model of coexisting interlayer distance in a single crystal can explain in a simple manner the ion-exchange catalytic effect of the sodium ion on the exchange of large cations by  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ . It was already mentioned that large cations cannot be taken up by crystalline zirconium phosphate because of steric hindrance. However we have found that large cations can be easily taken up by  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  if a small amount of a sodium salt is added to the external solution.<sup>43,44</sup> The  $\text{Na}^+$  ion behaves as a catalyst insofar as it is again found in the solution at the end of the ion-exchange process. As an example, direct  $\text{Mg}^{2+}/\text{H}^+$  exchange on  $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  is not possible, even at the pH of the saturated  $\text{Mg}(\text{OH})_2$  solution, since hydrated  $\text{Mg}^{2+}$  is a very large species and its dehydration requires high energy. However, if  $\text{Na}^+$  is added to the solution, the  $\text{Mg}^{2+}$  is easily taken up at about pH 4. Chemical analyses of the samples during the process showed that

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Table II  
Interlayer Distance of Some Organic Derivatives of  
Zirconium Phosphate

Intercalated species	Interlayer distance, Å	Ref
Ethanol	14.2	47
1-Butanol	18.7	47
Ethylamine	14.2	47
<i>n</i> -Butylamine	19.0	46-48
<i>n</i> -Decylamine	32.1	46, 47
Benzylamine	19.2	47
Pyridine	10.9	46

Na<sup>+</sup> was inside the exchanger and X-ray patterns showed the coexistence of three interlayer distances, 7.6, 9.9, and 11.8 Å, respectively.<sup>44</sup> At the end of the process the X-ray showed only the 9.9-Å interlayer distance, and all the added Na<sup>+</sup> was again found in the solution.

In Figure 4 is reported a schematic explanation of the Na<sup>+</sup> effect. Na<sup>+</sup> first replaces H<sup>+</sup> ion, giving the phase  $\text{HNa}\cdot 5\text{H}_2\text{O}$  (11.8 Å). Owing to the large interlayer distance of this phase, Mg<sup>2+</sup> can enter inside the crystal structure, giving the phase  $\text{H}_{0.5}\text{Mg}_{0.75}\cdot 4\text{H}_2\text{O}$  (9.9 Å). The replaced Na<sup>+</sup> moves toward the center of the crystal replacing H<sup>+</sup> in the  $\text{HH}\cdot\text{H}_2\text{O}$  and giving new  $\text{HNa}\cdot 5\text{H}_2\text{O}$  phase and so on. When all the initial  $\text{HH}\cdot\text{H}_2\text{O}$  has been consumed the Na<sup>+</sup> replaced by Mg<sup>2+</sup> again goes into solution.

**Exchange of Organic Cations and Intercalation of Polar Organic Molecules.** It is well known that polar organic molecules (such as alcohols, glycols, amines) can be intercalated within the layered structure of clay minerals, and at present a very large literature in the field of clay organic reactions exists.<sup>45</sup> In 1965 Michel and Weiss were able to intercalate aliphatic amines into crystalline insoluble acid salts of tetravalent metals<sup>46</sup> whose stable layered structure is a very attractive one as a model to study the interlayer organization of the adsorbed species. Generally bilayers of intercalated organic molecules are obtained, and the interlayer distances of some organic derivatives of zirconium phosphate are listed in Table II. Investigations on the exchange of positively charged organic species such as tetraalkylammonium, pyridinium, and the cationic forms of amino acids with the monosodium forms of zirconium phosphate as well as titration curves of the dihydrogen form of zirconium phosphate with organic bases have also been performed.<sup>47,48</sup>

**Other Layered Insoluble Acid Salts.** Particulars on the synthesis and properties of layered acid salts other than zirconium phosphate can be found in the references of Table I.

Many properties of these compounds are similar to those already discussed for zirconium phosphate. However, an accurate study of the relative changes of their properties as a function of the tetravalent metal and polybasic acid involved could be very interesting. A preliminary discussion of this aspect has been reported in ref 8. A recent investigation on layered titanium phosphate showed that its ion-exchange properties strongly depend on the preparation me-

thod.<sup>49</sup> For example, short- and long-refluxed samples of titanium phosphate, although showing very similar X-ray diffraction patterns, after titration with NaOH give two completely different monosodium forms. This phenomenon could be of a general nature for layered insoluble acid salts and deserve further attention.

### Fibrous Insoluble Acid Salts of Tetravalent Metals

The study of the cerium(IV)-phosphoric acid system is very complex since several crystalline precipitates can be obtained.<sup>50,51</sup> Of these, particularly interesting is a fibrous precipitate with formula  $\text{Ce}(\text{HPO}_4)_2\cdot 3\text{H}_2\text{O}$ .

By investigating the Th(IV)-phosphoric acid system, a fibrous thorium phosphate with properties very similar to cerium(IV) phosphate has also been obtained,<sup>52</sup> and it is very likely that other fibrous exchangers may be obtained in the near future. Fibrous insoluble acid salts are very interesting because they can be used to prepare inorganic ion-exchange papers, which have been already employed as chromatographic or electrophoretic supports.<sup>53</sup> Fibrous acid salts have also been utilized to prepare inorganic ion-exchange membranes without binder. The properties of these membranes have been reported in ref 54. Data have been collected on the ion-exchange properties of fibrous insoluble acid salts toward alkali, alkaline earth ions, Pb<sup>2+</sup>, and some transition-metal ions.<sup>55</sup> Very high selectivities for certain cations have been found. No discontinuous phase transition seems to occur. Unfortunately, the crystalline structure of the fibrous acid salts is yet unknown, and it is therefore difficult to give a reasonable interpretation of their ion-exchange mechanism.

### Crystalline Insoluble Acid Salts of Unknown Structure

Under appropriate experimental conditions several insoluble acid salts of unknown structure can be obtained. Some of these compounds are listed in Table III (see ref 56-65). The reader is referred to original

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Table III  
Some Insoluble Acid Salts of Tetravalent Metals Having a yet Unknown Structure

Formula	Theoretical ion-exchange capacity, mequiv of H <sup>+</sup> /g	First x-ray diffraction maximum, Å	References
Ti(HPO <sub>4</sub> ) <sub>2</sub> ·0.5H <sub>2</sub> O	8.04	9.2	56
Ti(HPO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	7.25	11.6	57-58
Zr(HPO <sub>4</sub> ) <sub>2</sub>	7.06	5.6	59
Zr(HPO <sub>4</sub> ) <sub>2</sub>	7.06	9.4	60
Zr(HPO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O <sup>a</sup>	6.27	12.2	60
Zr(HPO <sub>4</sub> )(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	13.1		61
Ce(HPO <sub>4</sub> ) <sub>2</sub> ·1.33H <sub>2</sub> O <sup>a</sup>	5.61	15.9	62
Ce(OH) <sub>x</sub> (PO <sub>4</sub> ) <sub>x</sub> (HPO <sub>4</sub> ) <sub>2-2x</sub> ·yH <sub>2</sub> O			51
Ce(HAsO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	4.36	10.1	63
Th(HAsO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O <sup>a</sup>	3.75	7.05	64
Th(HAsO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	3.63	8.21	65

<sup>a</sup> Needle shaped.

references for particulars on their preparation and properties. The crystalline structures being unknown, at present it is not possible to give a comprehensive account of their properties; however, some of these compounds exhibit interesting ion-exchange characteristics for practical application (see later), and therefore investigations on their crystalline structure are highly desirable.

### Applications

Insoluble acid salts can find practical application in many fields. An important application is their use as ion-exchange materials. In fact, compared to organic ion-exchange resins they present the advantage of a better resistance to temperature, to radiation, and to oxidizing solutions; compared to zeolites they present the advantage of higher resistance toward acid media. Ion exchange in molten salts<sup>66-69</sup> and applications in nuclear technology<sup>1,2</sup> are therefore possible. The discovery that large cations can be taken up by ionic forms with large interlayer distance has opened new developments. The selectivity of zirconium phosphate for polyvalent cations is very high, and analytical separation or concentration of these cations can be performed.<sup>8</sup> In our opinion practical application of ZrHPO<sub>4</sub>NaPO<sub>4</sub>·5H<sub>2</sub>O in water-softening could be also possible. Amorphous zirconium phosphate has been utilized in kidney machines for the removal of ammonium ions from blood.<sup>70</sup> Polyhydrated zirconium phosphate is a promising compound for removal of both the ammonium ion and ammonia from blood or waste solutions.<sup>71</sup> Owing to the discontinuous phase transition during exchange, insoluble acid salts can be also employed as solid pH buffers, while their salt forms could be used to maintain constant the ionic fraction of a pair of cations, such as Na<sup>+</sup>-K<sup>+</sup>, in solution.<sup>8</sup>

The surface properties of microcrystals of insoluble acid salts of tetravalent metals are also very important from both a fundamental and a practical point of view. It has been mentioned before that large species cannot diffuse, or diffuse very slowly, within the layered structure especially if it is narrow; as a consequence, in

many cases the ion exchange and the gas adsorption take place mainly on the surface. The number of surface fixed charges per gram of Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O can thus be easily determined by replacing the surface protons with a large cation<sup>72</sup> such as Cs<sup>+</sup>. This value depends on the particle size, which, in turn, depends on the preparation method of Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O. In the direct precipitation method the surface fixed charges are usually 0.07-0.1% of the total ones; however, the electrical conductance and the electrochemical properties of membranes consisting of Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O mainly depend on the surface counterions.<sup>54</sup> Furthermore, it is likely that the catalytic activity of layered insoluble acid salts essentially depend on the properties and extension of the surface. To date, only a few applications of the catalytic activity of layered exchangers are known. Kalman et al. have successfully employed the copper form of the zirconium phosphate for the oxidation of CO to CO<sub>2</sub> and potential employment in abatement in automobile pollution exists.<sup>73</sup> Recently zirconium phosphate has been loaded with several transition metal ions, and these materials are promising as catalysts.<sup>74,75</sup> La Ginestra, by partially reducing the copper form with hydrogen, has obtained a copper-hydrogen form containing dispersed Cu atoms.<sup>76</sup> Interesting applications of dispersed metal atoms in zirconium phosphate lattice may be expected.

Zirconium phosphate has been also employed as a support for gas-solid chromatography.<sup>77,78</sup> Interesting separations have been obtained by Allulli et al. with the K form of zirconium phosphate.<sup>78</sup>

Inorganic membranes consisting of insoluble acid salts are interesting from both a fundamental and a practical point of view.<sup>54,79</sup> They present a unique possibility of relating their electrochemical and osmotic properties to the known reticular arrangement of the fixed charges and counterions or to steric factors. On

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the other hand, owing to their stability, these membranes could find applications in particular processes in which organic membranes cannot be employed because of their higher degradability. Particularly promising could be their employment in fuel cells at high temperatures or in the concentration of wastes containing fission products.

Some acid salts with as yet unknown crystalline structures possess interesting ion-sieve properties; e.g., thorium arsenate behaves as a very narrow ion sieve and only H-Li exchange is therefore possible. This interesting property has already been employed for the separation of  $\text{Li}^+$  from other cations.<sup>64</sup>

The very high selectivity of fibrous cerium phosphate for  $\text{Pb}^{2+}$  and certain other divalent cations is also very promising for practical applications.<sup>44</sup> Finally, impregnated papers or thin layers of insoluble acid salts have been successfully employed for several chromatographic separations of inorganic cations.<sup>9,11,53,80</sup>

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### Future Developments

In recent years much progress in both fundamental and practical aspects of layered exchangers has been made; however, further investigations, especially on the reticular position of counterions and solvent, on the variation of the selectivity with interlayer distance are still needed in order to understand in detail their ion-exchange mechanism and to make some predictions about their ion-exchange properties.

Concerning fibrous as well as needle shaped acid salts the preparation of crystals large enough for structural determination is the first important step for future progress.

An understanding of the reasons for which a given crystalline structure is formed is of utmost importance, and studies in this field will be also very useful for the synthesis of new inorganic ion-exchange materials.

Finally, studies on the surface properties, on the catalytic activity, and on the diffusion and electrical transport of counterions could lead to some important new practical applications of these materials.

## Photochromism and Electrochromism in Amorphous Transition Metal Oxide Films

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Much attention has recently been given to the phenomena of photochromism and electrochromism since their proposed application<sup>1-3</sup> in information display devices. The phenomena basically consist of the ability of certain materials to change their light absorbing properties when optically excited (photo-

chromism) or while under the influence of an externally applied electric field (electrochromism). The induced coloration remains even after the excitation source has been removed. Technological interests result because the material returns to its original state upon either irradiation with light of the frequency corresponding to the induced absorption or by reversing the polarity of the externally applied electric field. Thus, the material behaves in a reversible manner, and it can be cycled at will. These phenomena, as first demonstrated by Pohl<sup>4</sup> with alkali halides, led to the present day concepts of color centers.<sup>5</sup> Current concepts of

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