

Inorganic Ion Exchangers

I. Acidity, Hydrolysis and Resistance to Acids of some Inorganic Ion Exchangers, Especially Zirconium Phosphate

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Among the basic salts proposed for use as ion exchangers, compounds of zirconium(IV) should generally be preferred to those of titanium(IV), as the latter ones are much more susceptible to hydrolysis. This involves not only a troublesome instability of the titanium ion exchangers even in acid solutions, but also a lower exchange capacity than for the corresponding zirconium compounds. Among these, the phosphate is considerably more resistant to strong acids than are the arsenate or tungstate, and seems therefore to be the best choice for acid media. Procedures allowing the preparation of zirconium phosphate gels of reproducible composition, and hence reproducible sorption properties, have been tried out. The products have ratios phosphate/zirconium varying from 1.05 to 1.98. For a few representative gels of various compositions, neutralization and hydrolysis curves have been determined. The neutralization curves reveal the gels as moderately acid ion exchangers, with the exchange sites up to at least $\text{pH} \approx 8$ entirely localized to the phosphate groups. Above $\text{pH} \approx 8$, an extensive hydrolysis sets in, making the gels unsuitable for ion exchange purposes within this region. The variations between the different gels, as regards the amounts of hydrogen and phosphate ions released for a certain value of pH , are what one would expect from the variations in their composition, as determined by gravimetric analysis.

The numerous and difficult separation problems connected with the re-processing of nuclear fuels have caused a revival of interest in inorganic ion-exchangers on account of their superior resistance to radiation and, as a rule, high thermal stability, as compared with organic ion exchangers.¹⁻¹³ An ion-exchanging material has, however, to possess several additional qualities in order to be a practically useful ion exchanger for the present purpose. The most important of these may be summarized as follows:

1. The material must be virtually insoluble within very wide limits of pH. Furthermore it should preferably be possible to use either in strongly acid or in fairly alkaline solutions, as such media are often encountered in reprocessing work.

2. The exchange capacity must be high enough to ensure a practical operation.

3. Sorption and elution must be so rapid that columns can be operated at reasonable flow rates. This means that the polymer network must be open enough to allow a sufficiently free diffusion of the exchangeable ions, *i.e.* the degree of cross-linking must not be too high.

4. The resistance to attrition must be so good that columns can be loaded and eluted many times without severe clogging or channelling.

5. The ion exchanger must be reproducible so that minor changes in the method or materials used for preparation do not cause major changes of performance.

6. The selectivity must be so high that a convenient separation between different ions, or at least types of ions, can be effected by suitable variation of pH. This is primarily achieved by choosing an ion exchanger whose functional groups possess widely varying affinity to the ions which are to be separated, which means that these ions should have widely varying abilities to enter into complex formation with the functional groups. The selectivity might be further improved by using an optimal degree of cross-linking for the polymer network of the ion exchanger. (*cf.* Ref.¹⁴, p. 169). As already has been pointed out, however, the degree of cross-linking must not be too high as this would imply inconveniently low sorption rates.

7. If a separation is to be accomplished by variation of pH, another condition is obviously that the ions to be sorbed are able to compete successfully with the hydrogen ion for the functional groups within the available range of pH, *i.e.* the acidity of these groups must be so high that they are not definitely blocked for other ions. Particularly the affinity to high-valent metal ions must be so strong that these are sorbed even from solutions which are acid enough, virtually to suppress the hydrolysis. For four-valent ions this means that sorption has to take place from solutions of an acidity around 1 M. Sorption from appreciably hydrolysed solutions is not desirable as the polynuclear species which as a rule predominate there are in most cases sorbed rather slowly.⁶ This may either depend on a slow diffusion of the bulky polymers, or on a preferential sorption of the monomers, which are formed only by slow depolymerization reactions. The latter explanation seems *a priori* quite reasonable, as the sorption would very likely be favoured by a high charge per central atom. In the case of zirconium (IV), it has been shown, however, that the polymers are more strongly sorbed than the monomers,¹⁵ so that in fact the first alternative is the more likely one. Evidently, the total charge of the ion to be sorbed is of greater importance than the average charge per metal atom forming part of it. A decrease of sorption with polymerization should therefore only be expected when the ionic aggregates are growing so large that the ion exchanger starts to act as a sieve.

Most of the conditions set forth above have to be fulfilled in most applications of ion exchangers. The demand for a high selectivity is, however, especially

important for the use intended here. The solutions to be treated are as a rule obtained by dissolving the spent nuclear fuel in concentrated nitric acid. They contain, besides uranium and plutonium, most elements between the atomic numbers 30 and 66 as fission products. Only nuclides still possessing a fair activity after a moderate cooling time, however, are of prime interest at the separations. Compilations of these, valid for various times of irradiation and cooling, have been given by several authors.¹⁶⁻¹⁹ Even after a reasonable cooling time of, say, three months, most types of cations are still represented among the active nuclides, *viz.* M^{4+} (Pu^{4+} , Zr^{4+}); M^{3+} (Y^{3+} , Ce^{3+} , Pr^{3+} and other lanthanon ions, possibly also Pu^{3+}); MO_2^{2+} (UO_2^{2+} , possibly PuO_2^{2+}); M^{2+} (Sr^{2+} , Ba^{2+}) and M^+ (Cs^+ , Rb^+). Niobium is present as hydrolysed species of seemingly unknown composition, most probably polynuclear and, at least in part, colloidal. The equilibria between these species adjust themselves only slowly, and the behaviour of niobium will therefore tend to depend upon the history of the solution.²⁰ This is even more true of ruthenium, which in the used medium exists as a series of inert nitrosyl-nitrato complexes.^{21,22}

Besides the products coming from the nuclear fuel, the solutions will in practice also contain components stemming from other sources. Most important among these are anions capable of forming complexes of some strength with the cations to be separated. Their presence may change considerably the order of affinities valid for a medium where no complexes are formed. Especially the sulphate ion should be considered, as it is added or formed during several reprocessing procedures in frequent use.^{23,24} If the fuel, or its protective canning, contains zirconium, fluoride solutions are as a rule used for dissolving, and fluoride ions will hence enter the process solutions.^{23,25}

The decanning, the corrosion of the process vessels (mostly made of stainless steel) and the addition of various reagents during the processing will also cause an introduction of further cations, such as Al^{3+} , Fe^{3+} , Ni^{2+} , Cr^{3+} , and Na^+ , in amounts large enough to warrant consideration, though they are inactive.

ION EXCHANGE PROPERTIES OF SOME HYDROUS OXIDES AND BASIC SALTS OF ELEMENTS IN REDOX STATE FOUR

Most of the species enumerated above as constituents of reprocessing solutions are cations. The majority moreover belongs to the class of acceptors termed (*a*). These are characterized²⁶ by an especially strong affinity to the first ligand atom in each group of the Periodic Table, *e.g.* to oxygen within Group VI, and also by a rapid increase of the affinity to a certain ligand as the ratio charge/radius of the acceptor grows. The acceptors of class (*b*), of opposite characteristics, have in fact only one typical representative, *viz.* ruthenium, while the alkali and alkaline earth ions hardly possess any marked acceptor properties at all.

The obvious way to effect a separation will therefore be by means of cation exchange and the best selectivity will be reached by exchangers possessing functional groups which show widely varying affinity to different class (*a*) acceptors. As the hydrogen ion is a typical (*a*) acceptor,²⁶ the functional groups will consequently have to be more or less basic, and presumably will a good selectivity even imply a fairly high basicity.

Now most of the inorganic ion exchanging materials, which have been found to fulfil at least acceptably the fundamental qualifications set forth

above for a useful ion exchanger, possess a negatively charged polymer network and are thus able to act as cation exchangers. Important among these are the hydrous oxides of silicium (silica gel), tin(IV) and zirconium(IV), and also a number of "basic salts" of metals in high oxidation states, particularly zirconium(IV) and titanium(IV).¹⁻¹³ The functional groups carrying the negative charge of the network are in all those cases markedly basic, though the basicity varies considerably between the different gels. The hydrous oxides contain only the strongly basic oxo-group whereas the characteristic groups of the "basic salts", *e.g.* phosphate, arsenate, or tungstate, are considerably less basic. Very often, however, a certain amount of oxo-groups is also present which results in polyfunctional ion exchangers, with a total exchange capacity equal to the sum of the various functional groups. In acid solutions however, this total capacity cannot be utilized, because the oxo-groups will soon be completely blocked by hydrogen ions as the acidity increases. The exchange will then occur only at the less basic groups and the exchange capacity in acid solutions will therefore be determined by the number of these.

On account of the higher basicity of their functional groups, the hydrous oxides may thus be presumed to be more selective than the basic salts, but for the same reason, they are apt to sorb cations poorly in acid solutions. This may make them unsuitable for the sorption of easily hydrolysed ions.

The basic properties of the hydrous oxides may even be so pronounced that further hydrogen ions are taken up by the functional groups, though counterions enough to balance the negative charge of the network have already been co-ordinated. The ion exchanger will then acquire a positive charge, which necessitates the sorption of an equivalent amount of counter-anions from the solution. These are easily exchangeable, and the polymer will therefore act as an anion exchanger in solutions which are sufficiently acid to bring about such an extra uptake of hydrogen ions. The exchange capacity for anions will evidently grow with the acidity. Simultaneously the cation exchange capacity will decline on account of the increasing competition from the hydrogen ions. An ion exchanger of the amphoteric character described will therefore mainly act as an cation exchanger in alkaline and as an anion exchanger in acid solutions, whereas in an intermediate range of pH both cation and anion exchange properties will be exhibited.^{1,2}

The actual course of the cation and anion exchange capacity as a function of pH will depend upon the basicity of the consecutive protolytic steps of the functional groups. Thus among the hydrous oxides mentioned above, zirconium hydroxide^{1,2} is the most basic one, displaying a perceptible anion uptake up to $\text{pH} \approx 6$ when shaken with solutions containing sodium chloride and hydrochloric acid, or sodium hydroxide, to an essentially constant ionic strength=0.1 M. In fact, equal amounts of Cl^- and Na^+ are sorbed¹ at $\text{pH}=6.7$. For tin(IV) hydroxide, which is markedly less basic, this point has moved¹ to $\text{pH}=4.7$. Silica gel, finally, shows no amphoteric behaviour at all. If saturated with hydrogen ions, and then carefully washed until no acid can be detected in the washings, it does not afterwards take up further hydrogen ions,⁶ not even from 1 M nitric acid.

Containing less basic functional groups than the hydrous oxides, the basic salts show little tendency to act as anion exchangers, even in strongly

acid solutions. Instead they still exhibit a high cation exchange capacity in such solutions. This should *a priori* make them especially suitable for the sorption of easily hydrolysed ions. It may be suspected, however, that the sorption of very high-valent ions occurs irreversibly, as these are likely to have an affinity to the functional groups which is comparable with that displayed by the central ion building up the polymer network. Thus considering an extreme case, it is hardly to be expected that Zr^{4+} , sorbed on zirconium(IV) phosphate, would be possible to remove without the destruction of the ion exchanger. In such cases, where no reversible ion exchange takes place, the basic salts rather act as precipitation carriers. As such, they had in fact found important use even before being tried as ion exchangers.²⁷

In summing up it may be said that inorganic ion exchangers of rather different properties are available, and the best choice depends upon the nature of the separation to be performed. If a very high selectivity is required, a fairly low acidity has to be tolerated, and *vice versa*.

CHOICE OF ZIRCONIUM PHOSPHATE FOR USE IN ACID SOLUTIONS

One aim of this investigation has been to find inorganic ion exchangers capable of sorbing easily hydrolysed ions from strongly acid solutions. As has been pointed out above, such ion exchangers have to be fairly acid and the attention has therefore been focused on the basic salts of zirconium(IV) and titanium(IV), which are formed as gelatinous precipitates when mixing the components. Several of these gels also possess the necessary qualification of being virtually insoluble just in strongly acid solutions. On the other hand, the basic salts are apt to hydrolyse as pH is raised, and above a certain value of pH, characteristic for each salt, the hydrolysis rapidly becomes conspicuous. The upper limit of pH for a successful application of the ion exchanger in question has then evidently been reached.

Now it is well known that titanium(IV) is much more easily hydrolysed than is zirconium(IV). The anions will therefore come off at a much lower value of pH for a titanium salt than for the zirconium salt of analogous composition. Likewise, if basic salts are prepared of both metals from solutions of the same pH and concentration of anion, the zirconium salt ought to contain rather more anions per metal atom. This has been verified in the present investigation by a comparison between phosphates of zirconium(IV) and titanium(IV) prepared analogously (see description below). The molar ratio phosphate/metal on mixing, AM, was chosen = 2.0. After that equilibrium had been reached between the precipitates and the supernatant solutions, the latter were analysed and the actual molar ratios in the precipitates hence determined. While in case of zirconium this ratio, $(P/Zr)_i$, varied between 1.87 and 1.94 (Table 1), it was found for titanium to be much lower, *viz.* $(P/Ti)_i = 1.03, 0.97, \text{ and } 1.02$ for three preparations made. Even if AM for titanium phosphate was chosen as high as 5.0, the ratio $(P/Ti)_i$ only reached a value of 1.21. The exchange capacity in such media, where the oxo-groups are still blocked, will therefore be considerably lower for the titanium phosphate, as has in fact been confirmed by the measurements of Gal and Gal.³ They found that the uptakes of Na^+ and UO_2^{2+} at a certain value of pH were about

three times larger on a certain preparation of zirconium phosphate than on a titanium phosphate prepared in a similar way.

The strong tendency to hydrolyse and, consequently, the low exchange capacities exhibited by basic salts of titanium(IV), make them rather less promising as ion exchangers than the corresponding zirconium salts, especially as these seem to be more resistant to attrition.

Basic salts of zirconium(IV) have been prepared with phosphate, arsenate and tungstate as anions. In the case of phosphate and tungstate, various ways of preparation have been tried. It may be expected that the proportion anion/metal (AM) used at the precipitation of the gel, and also the acidity of the solutions to be mixed, would be important for the composition and sorption properties of the final product, and this has also been confirmed. Furthermore, the way of washing and drying the gel has turned out to be of importance. Thus the sorption rate, especially of high-valent ions, depends very much upon the water content of the gel, as will be discussed in next paper of this series. Details about the preparation of all gels used are given below.

The resistance to strong acids of a few representative zirconium gels was investigated by shaking them for 24 h with acid of varying concentration C_H . After centrifuging, a sample of the clear solution was evaporated and the residue ignited and weighed. The action of nitric acid was studied most extensively. Zirconium phosphate gels representing all the values of AM employed, viz. 1.4, 2.0, and 3.0 (cf. Table 1) were investigated and also one arsenate and one tungstate gel. These were both prepared with AM=2.0 The tungstate gel was the one prepared at high pH (cf. p. 715). The results, Fig. 1, show that phosphate gels are very resistant towards nitric acid, and this applies especially to the gels rich in phosphate, prepared with AM=2.0 and 3.0. For the gel of AM=1.4, a marked dissolution begins at acid concentrations >4 M. The arsenate, and even more the tungstate, are on the other hand dissolved quite considerably, as the concentration of nitric acid is increased. For strongly acid solutions, phosphate gels are thus to be preferred before gels containing

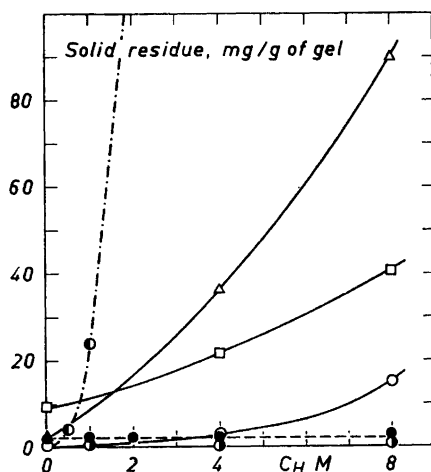


Fig. 1. Resistance to strong acids of various basic zirconium salts. The gels have been shaken for 24 h with the respective acid, $v/m=10$ ml/g. The ignited residue from the clear solutions, per g gel employed, is plotted as a function of the concentration of acid. The symbols refer to: 1) Nitric acid: □ arsenate; △ tungstate; ○ phosphate 1.4-II (all with full drawn curves); ● phosphate 2.0-IV and 3.0-IV (curve of dashes); 2) Perchloric acid: ● phosphate 1.4-II (no curve drawn). 3) Sulphuric acid: ● phosphate 1.4-II (curve of dots and dashes). The phosphate gels contained about 50 % water, the arsenate and tungstate gels about 30 %.

arsenate or tungstate. Even these are, however, very slightly soluble in comparison with the hydrous zirconium oxide which is reported² to be completely dissolved in strong acids of a concentration > 0.1 M.

The phosphate gels were also treated with perchloric and sulphuric acid. The former acts in about the same way as nitric acid, with the notable exception that even 8 M perchloric acid does not markedly dissolve the gel 1.4-II while 8 M nitric acid does, Fig. 1. The generally low dissolving power of these acids depends upon the fact that neither the nitrate, nor the perchlorate ion forms any strong complexes with zirconium(IV), able to compete seriously with the hydroxide or phosphate groups already present. The fact that high concentrations of nitric, but not perchloric, acid do dissolve at least gels low in phosphate suggests, however, that the nitrate ion has a slight tendency to form complexes, which is seemingly not the case for the perchlorate ion. This is also in keeping with the general experience about the complex forming ability of these ions. The sulphate ion, on the other hand, is known¹⁵ to form rather strong complexes with zirconium(IV), and sulphuric acid might thus be expected to dissolve the gels easier, in virtue of the combined action of its hydrogen and sulphate ions. A very extensive dissolution also occurs if the phosphate content of the gel is low, Fig. 1. The gels rich in phosphate, prepared with AM=2.0 or 3.0, are, however, dissolved only modestly (about 50 %) more by sulphuric than by nitric or perchloric acid (not presented in Fig. 1) A high content of strongly bound phosphate ions thus protects the gels from the attack of sulphate ions. As the composition of the gel approaches that of zirconium hydrous oxide, it becomes increasingly vulnerable, the hydrous oxide itself being readily dissolved by sulphuric acid.

The phosphate gels thus seem to be the most promising ones for separations in acid solutions. Among these, the gels richest in phosphate are most resistant to acids, but the differences between gels of various compositions do not seem large enough to warrant an exclusion of those low in phosphate from further studies. Only an investigation of all pertinent sorption properties of the various phosphate gels will secure the best choice for each particular separation problem.

PREPARATION AND ANALYSIS OF THE ION EXCHANGERS TRIED

Zirconium phosphate. The following procedure was finally adopted as a convenient way for the preparation of gels of fairly reproducible compositions and sorption properties. A 0.3–0.4 M solution of zirconyl nitrate, containing 1 M nitric acid, was precipitated with a phosphoric acid solution of about the same volume. In order to get gels of various phosphate contents, three different ratios AM were used, viz. 1.4, 2.0, and 3.0, Table 1. In the later preparations, the composition of the freshly precipitated gel ($(P/Zr)_i$, First, of Table 1) was then determined by analysis of the supernatant solution. No zirconium was left there. As to phosphate, very little remained for AM=1.4, while a considerable part was still in solution for AM = 2.0 and 3.0. Nevertheless the phosphate content of the gels increased considerably with AM. For the last preparations with AM=2.0 and 3.0, it was further investigated if the surplus of phosphate would change when being in contact with the gel. Samples of the solution were therefore taken at regular intervals, and after each sampling the gel and the solution were thoroughly mixed in order to facilitate equilibration. It was found, that the gel became richer in phosphate during this treatment. After a few days, however, equilibrium was reached ($(P/Zr)_f$, Final, of Table 1). These final values are considerably higher than those found for the fresh

Table 1. The ratio P/Zr at different stages of preparation of the gels. The phosphate content of the final products, for some gels compared with the amount of phosphate released at pH=14 and the amount of H⁺ released at the inflexion point. The ratio H⁺/P between the amounts of H⁺ and phosphate released from the gels at pH = 14.

Gel	AM	(P/Zr) _I		(P/Zr) _S	P* mmole/ g gel	P** release pH 14	H ⁺ /P release pH 14	H ⁺ release inflex.
		First	Final					
1.4-I-1	1.4	—	—	1.12	2.76	2.7	3.5	3.0†
1.4-I-2	»	—	—	1.05	2.66	—	—	—
1.4-I-3	»	—	—	1.15	2.81	—	—	—
1.4-II	1.43	1.41	—	1.22	2.91	—	—	—
2.0-I	2.0	—	—	1.58	3.36	—	—	—
2.0-III	2.02	1.86	1.94	1.73	3.51	—	—	—
2.0-IV	1.95	1.63	1.87	1.80	3.59	—	—	—
2.0-V	2.05	1.65	1.94	1.75	3.54	3.5	3.5	3.6††
3.0-I	3.0	1.86	—	1.89	3.67	—	—	—
3.0-II	3.05	2.10	—	1.95	3.73	3.8	3.4	4.3††
3.0-III	3.05	2.10	2.21	1.98	3.75	—	—	—
3.0-IV	3.09	1.84	2.15	1.94	3.72	—	—	—

* Calculated from (P/Zr)_S for gels containing 50 % water.

** Found from Fig. 3 for gels containing 50 % water.

† Read from Fig. 2 (varying I).

†† Read from Fig. 4 (I = 0.1 M), and then corrected to a water content of 50 %.

precipitates. Thus it is wise to wait until equilibrium has been reached, if a certain value of AM is to result in gels of one and the same composition. The gels are separated from the solutions by centrifuging and then, without previous washing, dried under infrared lamps, until a sample loses only 60 % of its weight on ignition. On this point, the gels are rather hard and brittle and are easily crushed into a coarse powder, which is washed free from fines and adhering mother liquor with distilled water. The washing is considered complete when pH of the washing fluid in equilibrium with the gel reaches a value about 3.5. Being due to a slight hydrolysis of the gels, this slightly acid reaction persists on further washing. The gels are then dried again, as a rule to a water content of 50 %, and screened. For the sorption experiments, a granular size of 60–100 mesh has been used. Certain gels have also been dried further, or even ignited, mainly for investigations of the influence of variations in water content on the sorption rate of different ions, which will be reported in the next paper of this series.

The partial hydrolysis during the washing makes an analysis of the final products necessary in order to establish their actual composition (*cf.* Ref.¹⁰). This is done by complete hydrolysis, most conveniently achieved by treatment with 2 M sodium hydroxide in a plastic beaker. If glass is used, dissolved silica interferes with the following phosphate analysis. The resulting hydrous oxide is washed free from alkali by strong ammonia solution, ignited and weighed as ZrO₂. In the filtrate, phosphate is precipitated as MgNH₄PO₄, which is then ignited and weighed as Mg₂P₂O₇. Sometimes, the zirconium hydrous oxide has been dissolved in 6 M nitric acid and reprecipitated with concentrated ammonia solution before ignition. In a few instances, MgNH₄PO₄ has also been dissolved (in dilute hydrochloric acid) and then precipitated again. These further treatments improved the look of the ignited precipitates which now turned out without the greyish discolouration noticed when no reprecipitation was undertaken, but the analytical

results did not deviate significantly from those found by the simpler procedure which was therefore judged to be adequate. Evidently that co-precipitation of Na^+ which may have been feared under the prevailing conditions (*cf. e.g.* Refs.^{1,28}) for both precipitates does not occur to any appreciable extent. In the case of zirconium hydroxide, this is presumably due to a displacement of the sodium ions during the ammonia wash. The ratios phosphate/zirconium found for the final products, $(\text{P}/\text{Zr})_s$, are as expected considerably lower than $(\text{P}/\text{Zr})_l$ for the gels in equilibrium with their respective mother liquors, Table 1. We have not, however, been able to confirm the results of Baetslé and Pelsmaekers,¹⁰ that all preparation starting with $\text{AM} > 1.67$ will end up with one and the same value of $(\text{P}/\text{Zr})_s = 1.67$. Our preparations with $\text{AM} = 3.0$ are by far not that much hydrolysed. On the other hand we find that even if AM is as low as 1.4, further hydrolysis sets in on washing, which is also contrary to the findings of Baetslé and Pelsmaekers.¹⁰

Zirconium arsenate was prepared analogously from zirconyl nitrate and arsenic acid, but only one ratio of AM was used, *viz.* 2.0. This gel was finally dried to a water content of 30 %.

Zirconium tungstate was prepared in two different ways, resulting in gels with very different sorption properties, as will be reported in the next paper of this series. For the first preparation, a 0.3 M solution of zirconyl nitrate in 1 M nitric acid was precipitated with a 0.6 M sodium tungstate solution, acidified so as to have a value of $\text{pH} = 1.95$ (measured by a quinhydrone electrode) which is close to the value where tungstic acid precipitates. After one day in contact with the mother liquor, the gel was centrifuged, dried and washed in the manner described for zirconium phosphate. For the second preparation, the zirconyl nitrate was instead dissolved in water and precipitated with a sodium tungstate solution of the rather high value of $\text{pH} = 4.20$. The following treatment of the gel was the same as above. In both preparations, the ratio AM was kept at 2.0 and both gels were finally dried to a water content of 30 %.

Titanium phosphates were prepared with ratios $\text{AM} = 2.0$ and 5.0 by precipitating a 0.3 M solution of titanium chloride in 2 M hydrochloric acid with 0.5 M and 1.25 M solutions of phosphoric acid, respectively. After three days, the supernatant solutions were analysed with the results indicated above (p. 711).

ACIDITY AND HYDROLYSIS OF ZIRCONIUM PHOSPHATE GELS OF VARIOUS COMPOSITIONS

The acidity of a few representative zirconium phosphate gels was investigated by determination of their protolysis curves. This was done by shaking certain amounts of gel, m , with certain volumes, v , of solution containing various concentrations of sodium hydroxide, or perchloric acid, until equilibrium had been reached, and then determining the amounts of hydrogen ions released from the gels as a function of pH . Simultaneously the hydrolysis was studied by the determination of the phosphate concentration of the equilibrium solutions. In order to avoid contamination with silicic acid, all strongly alkaline solutions were shaken in plastic bottles. The number of hydrogen or phosphate ions released from a unit weight of gel at a certain value of pH evidently depends upon the value of the ratio v/m , as soon as the composition of the solution, or the gel, is markedly changed by the reactions taking place. This will inevitably happen in the present measurements which just aim at the determination of very high degrees of exchange and hydrolysis. Curves presenting the neutralization or hydrolysis of a certain gel will therefore only be valid for a specified value of v/m , which has here been chosen = $100 \text{ ml} \cdot \text{g}^{-1}$ for all solutions with an equilibrium value of $\text{pH} > 2$, and = $10 \text{ ml} \cdot \text{g}^{-1}$ for more acid solutions (which are rather few).

In the first series, comprising three different gels, the ionic strength of the solutions was allowed to vary with the concentration of alkali or acid employed. Along the curves of Figs. 2 and 3, the medium thus changes from approximately 1 M sodium hydroxide to 1 M perchloric acid (for the neutralizations curves; the phosphate curves have been interrupted at $\text{pH} = 2$). In the intermediate range of pH the ionic strength is quite low. These curves are of interest especially from a practical point of view. Theoretically, it may, however, be more profitable to study the neutralization and hydrolysis at a constant ionic strength. This has been done for two gels of high values of $(\text{P}/\text{Zr})_s$, at $I = 0.1 \text{ M}$, with sodium chloride as the supplementary salt, Figs. 4 and 5.

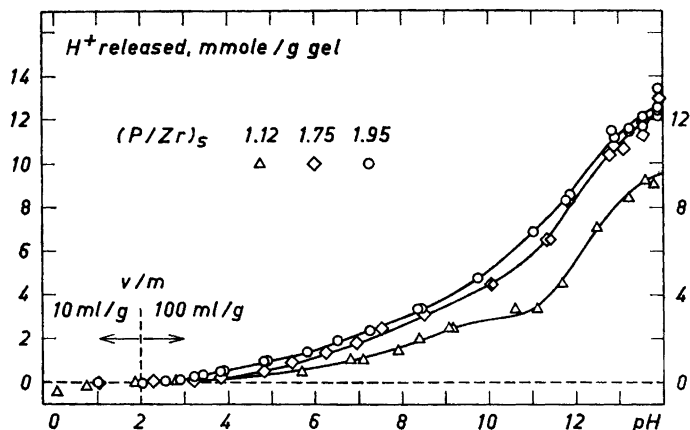


Fig. 2. Neutralization curves for zirconium phosphate gels of various compositions, all curves referring to gels containing 50 % water. Ionic medium varying along the curves.

The amounts of hydrogen and phosphate ions released were determined by titrating samples of the equilibrium solutions, freed from the gel by centrifuging, to the phosphate equivalence points around $\text{pH} = 9$ and 4.5 . A few such titrations were first performed potentiometrically, confirming that phosphate was the only weak protolytic system present. In the following the points of equivalence could therefore be indicated by phenolphthalein and methyl red, respectively. Even better than methyl red was methyl purple which has the very narrow pH range $4.8-5.4$. If the alkaline solutions were titrated directly with acid, both points of equivalence could be found in one titration. That no significant amounts of carbon dioxide entered even fairly alkaline solutions during such a titration was checked by performing a few titrations from the acid side. In this case the alkaline sample was rapidly added to a solution containing an excess of acid which was then titrated with standard alkali. The method entails the use of two samples for

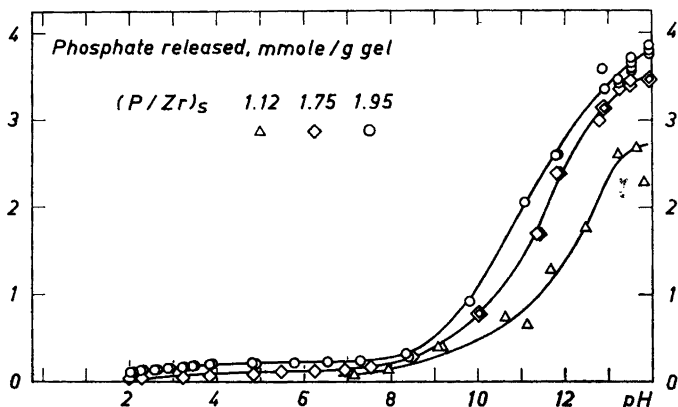


Fig. 3. Phosphate released to the solution as a function of pH for zirconium phosphate gels of various compositions. All curves refer to a ratio $v/m = 100$ ml/g gel and to gels containing 50 % water. Ionic medium varying along the curves.

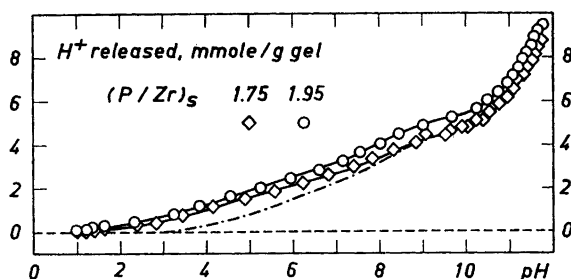


Fig. 4. Neutralization curves for zirconium phosphate gels of two different compositions in a medium where I has been kept ≈ 0.1 M (by addition of sodium chloride). The curves refer to $v/m = 100$ ml/g and to gels containing 40 % water. For comparison, the curve of the gel of $(P/Zr)_s = 1.75$ for varying ionic medium (from Fig. 2, corrected to 40 % water) has also been drawn (dots and dashes).

each determination as only one point of equivalence can be reliably found for each titration. The results from direct and back titrations agreed very well.

For strongly alkaline or acid solutions, also the value of pH could be reliably calculated from the titrations. For solutions where a protolysis of the phosphate system takes place, pH was instead measured by a glass electrode. The type of electrodes used (Radiometer, Copenhagen, Type B) has a slope very close to the theoretical value demanded by Nernst's law. This was, moreover, checked by measuring the value of pH of the following solutions: (a) 0.01 M HCl, 0.09 M NaCl (b) 0.01 M NaOH, 0.09 M NaCl. If the asymmetry potentials of the electrodes were corrected for in the way prescribed, by means of a phosphate buffer of pH = 6.50, several electrodes gave a mean value of pH for those solutions of (a) 2.07 ± 0.01 (b) 11.98 ± 0.02 . In a medium of $I = 0.1$ M, the measured value of pH will thus be quite close to the actual value of $-\log [H^+]$, especially within the alkaline range. Before the measurement of pH, solid sodium chloride was therefore added to all solutions which did not already contain it, to a total ionic strength of 0.1 M, in order to establish conditions similar to those prevailing at the calibrations. This also seemed advisable in order to minimize the liquid junction potentials within the galvanic cell. Admittedly a change of activities occurred simultaneously. This will not alter the course of the curves of Figs. 2 and 3 very much, however, as can be concluded from measurements undertaken with some of the solutions without previous addition

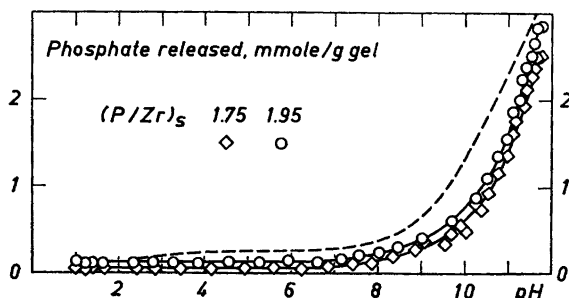
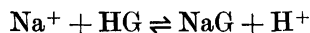


Fig. 5. Phosphate released to the solution as a function of pH for zirconium phosphate gels of two different compositions in a medium where I has been kept ≈ 0.1 M (by addition of sodium chloride). The curves refer to a ratio $v/m = 100$ ml/g gel and to gels containing 40 % water. For comparison, the curve of the gel of $(P/Zr)_s = 1.95$ for varying ionic medium (from Fig. 3, corrected to 40 % water) has also been drawn (dashed).

of salt. In the medium range of pH, between 5 and 11, the values then read were about 0.3 pH-units higher than those found after the addition of salt. For lower and higher values of pH, the difference soon became insignificant.

The gels behave as moderately acid ion exchangers, Figs. 2 and 4. They are much weaker acids than sulphonated organic resins, but on the other hand much stronger than all hydrous oxides investigated so far,^{1,6*} as could be foreseen from the less basic nature of their functional groups (*cf.* p. 710). The number of hydrogen ions released per g gel, and hence the exchange capacity for a certain value of pH, increase with the ratio $(P/Zr)_s$, which is just what to expect if the ion exchange takes place at the phosphate groups.

The addition of sodium chloride will of course displace the exchange equilibrium

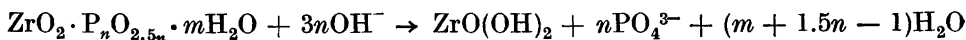


towards the right, and hence increase the release of hydrogen ions, as is also proven by the course of the curves of Fig. 4 (*cf.* Ref.¹⁴, p. 86).

As pH exceeds 9 or 10, all the neutralization curves rise much steeper than before. Simultaneously, however, the zirconium phosphates are extensively hydrolysed, Figs. 3 and 5. For the highest values of pH used, the hydrolysis even seems to approach completion, as is evident from Fig. 3. In fact, virtually all phosphate has been released at pH=14, as can be deduced from a comparison of the values for released phosphate, found from Fig. 3, with the total phosphate content calculated from the gravimetric analysis of the gels, Table 1.

In contact with the solutions of $[Na^+] = 0.1$ M, the gels are markedly less hydrolysed than if no extra salt is added, Fig. 5. The exchange of H^+ for Na^+ evidently makes the phosphate groups less liable for hydrolysis, which may be of practical interest.

If it is presumed that the hydrolysis results in zirconium hydrous oxide and orthophosphate ions, then the following formula should be valid, whatever structure the phosphate may have:



where $n = (P/Zr)_s$ and $m =$ moles water/mole zirconium in the gel, irrespective of the way the water is bonded, which is at present in dispute.²⁹ If this formula is correct, then the amount of OH^- consumed has evidently to be three times larger than the amount of phosphate released. The former quantity is equal to the amount of H^+ released which can be read from Fig. 2. The ratio of H^+ released to phosphate released, H^+/P of Table 1, is in fact not very far from the expected value of three, but nevertheless significantly higher. This additional release of H^+ is evidently due to the cation exchange properties of the formed hydrous oxide gel^{1,2} which are quite prominent at such a high value of pH as 14.

Both the neutralization curves of Fig. 4, and also the lowest one of Fig. 2, show a more or less pronounced inflexion point at a pH between 9 and 10.

* This will not be invalidated by the fact that the curve of silica gel in Fig. 3 of Ref.⁶ will be revised for $pH > 9$.

These points are reached after a release of H^+ not very far from the amount of phosphate present. Thus in Fig. 2, the release of H^+ at the inflexion occurring for $(P/Zr)_s=1.12$ is found to be 3.0 mmole/g gel, while from Fig. 4 the corresponding figures for the gels richer in phosphate are read as 4.3 and 5.2 mmole/g gel, respectively. These latter figures refer to gels containing 40 % of water and have thus to be recalculated to a water content of 50 % in order to be comparable with the previous ones.* The result is reported in the last column of Table 1. Considering the influence of the final steep rise of the neutralization curves on the position of the inflexion points, it seems quite likely that the amount of H^+ released during the first part of the process, involving no hydrolysis, is in fact equivalent to the phosphate content. The conclusion would be that the points of inflexion indicate the complete conversion of one protolysis step into the next one, whether this involves the transformation of dihydrogen into monohydrogen groups, or of monohydrogen groups into groups containing no hydrogen. As will be shown in papers to follow in this series, this dissociation is accompanied by an uptake of cation from the solution, equivalent to the amount of H^+ released, *i.e.* a practically ideal cation exchange is taking place. Contrary to that, the further consumption of H^+ beyond the inflexion point involves a successive break-up of all the bridges joining zirconium to phosphorus, finally resulting in a complete hydrolysis of the phosphate gel, as has been demonstrated.

For values of pH higher than 8 or 9, the hydrolysis of the zirconium phosphate gels will be so extensive as to prohibit their use as ion exchangers. Even for $pH < 8$, gels rich in phosphate still exhibit a perceptible hydrolysis, Figs. 3 and 5, though too slight to be likely to interfere with their practical utility.

As to the gel of the lowest phosphate content, a significant uptake of H^+ is found in strongly acid solutions, Fig. 2. The gel possessing a composition closest to that of the hydrous oxide thus retains at least a trace of the amphoteric behaviour so characteristic of the latter compound.

This work has been performed under a contract with *AB Atomenergi (The Swedish Atomic Energy Company)*, Stockholm, whose generous support is most gratefully acknowledged.

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* That such recalculations are allowed between these two percentages of water has been verified experimentally (to be reported later).

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Received December 3, 1963.