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MECHANISM OF ISOTOPIC EXCHANGE IN A HETEROGENEOUS SYSTEM

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SUMMARY

Using the ^{32}P isotope, the exchange of phosphate ions between zirconium phosphate and aqueous solution has been investigated. The exchange proceeds through two measurable processes whose rates differ by a factor of about ten, followed by an extremely slow third process. Of the two measurable processes, the faster one involves the phosphate groups at the surface of the solid while the other can be assigned to the interior phosphate groups. The mechanism of the surface process involves the hydrolysis of the phosphate groups at the surface followed by exchange between the phosphate groups and the hydrolysed material. The mechanism of the second process assigned to the interior phosphate groups involves the same chemistry as the surface reaction, the process being slower owing to the slower rate at which the aqueous phase comes into contact with the internal phosphate groups.

INTRODUCTION

The kinetics of the heterogeneous isotopic exchange reaction and ion-exchange reaction have been investigated during the last few decades and different mechanisms have been proposed by different workers. The kinetics of a heterogeneous reaction between a solid phase and solutions have been interpreted in terms of two rate processes^{1,2}. The faster process is reported to occur by the reaction of the groups at the surface of the solid^{1,3}, while the slower process is reported to occur by the reaction of the interior groups controlled either by a recrystallization mechanism⁴⁻⁷ or a self-diffusion mechanism⁷⁻¹⁰.

BOYD *et al.*¹¹ developed equations for evaluating the rate-controlling process in heterogeneous ion-exchange reactions and REICHENBERG¹² extended this work. Some limitations of applying the BOYD equations and REICHENBERG tests have recently been observed by HELFFERICH and co-workers¹³⁻¹⁶ and others^{17,18}. In a recent paper¹⁹, we reported the heterogeneous exchange reaction of phosphate ions between aqueous

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solution and solid zirconium phosphate¹⁰. The reaction was very slow and was followed for 250 h; this study revealed two rate processes. Later, the reaction was followed for 2500 h in terms of more parameters and the results are reported in this paper.

EXPERIMENTAL

Materials

Zirconium phosphate was a Bio-Rad product of different particle sizes. The solid was converted to the H⁺ or K⁺ form by eluting it with 1.0 M HCl or 1.0 M KCl. By chemical analysis, the composition of the product was found to be ZrP₂O₇ · 2.5H₂O. The aqueous solutions were prepared from analytical grade orthophosphoric acid. The radioactive tracer used was the ³²P isotope of high specific activity obtained from the Radiochemical Centre, Amersham, Bucks., Great Britain.

Determination of surface area

The relative surface areas of the samples used were determined by measuring the extent of adsorption of dye from a solution of Brilliant Cresyl Blue, as described by PATERSON²⁰. The samples were previously pre-treated under conditions identical with those for the kinetic experiments described below.

Kinetic runs

In each experiment, a known amount of zirconium phosphate, after pre-treatment with either water or an aqueous solution of phosphate, was brought into contact with a known amount of a labelled solution of phosphate. The distribution of isotopes under different conditions was followed by determining the activity of an aliquot of the solution. An Ekco Electronics Ltd. Endwindow G.M. counter was used together with an Isotope Developments Ltd. Scaler 1700 instrument.

The count-rate was corrected for dead-time and radioactive decay. The results were expressed in terms of the exchange fraction F with time according to the expression

$$F = \frac{S_0 - S_t}{S_0 - S_a}$$

where F = fraction exchanged at time t , S_0 = counts/sec/ml at $t = 0$, S_t = counts/sec/ml at $t = t$, and S_a = calculated counts/sec/ml assuming 100% exchange. If, in this system, P_a and P_s are the initial amounts in moles of phosphate ion in the aqueous and the solid phases, respectively, A_s is the total activity of the system, and V is the volume of the liquid phase, then

$$S_a = \frac{P_a}{P_a + P_s} \cdot \frac{A_s}{V}$$

The calculated values of S_a were corrected for volume and activity loss from the system due to samplings.

For hydrolysis and the reverse exchange, the solid was labelled to different extents by allowing the direct exchange reaction to occur for different lengths of time. Then the liquid phase was carefully sucked out and the solid was washed twice with

small amounts of distilled water. The non-active liquid solution was brought into contact with the labelled solid and the activity was followed with time.

In the reverse exchange, as the phosphate ions in the solid phase could not be labelled to the extent of 100%, the activity flows in two opposite directions, whereas in the direct exchange the activity flows in one direction until isotopic equilibrium is reached. Therefore, the amount of the phosphate ions in the solid phase involved in the reverse reaction does not remain constant. As a result, the calculation of the factor $(P_a)/(P_a + P_s)$ is complicated and cannot be evaluated exactly. However, calculations have been made for a hypothetical case, considering that 100% of the phosphate ions in the solid phase were involved.

The rates of the individual process were calculated by applying the reaction half-time for an individual process obtained by resolution of the MCKAY plot²¹ as shown later in Fig. 2. The rates R_I and R_{II} for the processes I and II can be expressed by the following equations:

$$R_I = \frac{(P_s \times F_I) \times P_a}{(P_s \times F_I) + P_a} \times 0.693 \times \frac{1}{I t_{\frac{1}{2}}}$$

$$R_{II} = \frac{(P_s \times F_{II}) \times P_a}{(P_s \times F_{II}) + P_a} \times 0.693 \times \frac{1}{II t_{\frac{1}{2}}}$$

where F_I and F_{II} are the exchange fractions for processes I and II and $I t_{\frac{1}{2}}$ and $II t_{\frac{1}{2}}$ the reaction half-times for processes I and II, respectively.

RESULTS AND DISCUSSION

That the exchange is reversible is indicated in Fig. 1, which shows the typical results of the kinetic runs. The count-rates were normalized so that the total activity in the system was the same at the start of the direct, the reverse and the hydrolysis reactions. Although in our previous paper¹⁰ it was reported that the exchange reaction involves the contributions of two rate processes only, the resolution of the MCKAY plot in Fig. 2 shows that the reaction consists of at least two rate processes followed by a extremely slow third process.

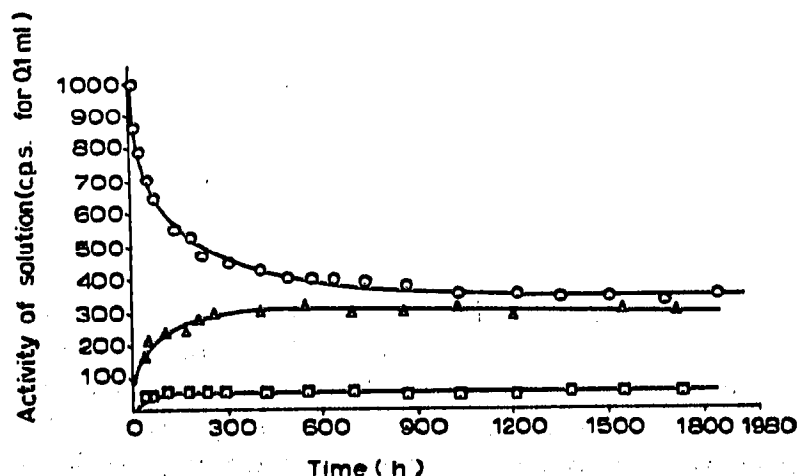


Fig. 1. Some typical kinetic runs, O, ZrP + labelled phosphate solution; Δ, labelled ZrP + phosphate solution; □, labelled ZrP + water.

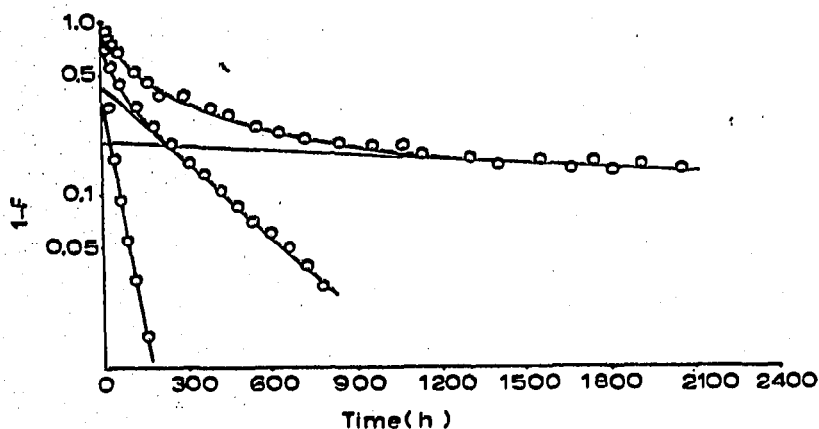


Fig. 2. A typical McKay plot showing analysis into three straight lines. F = exchange fraction

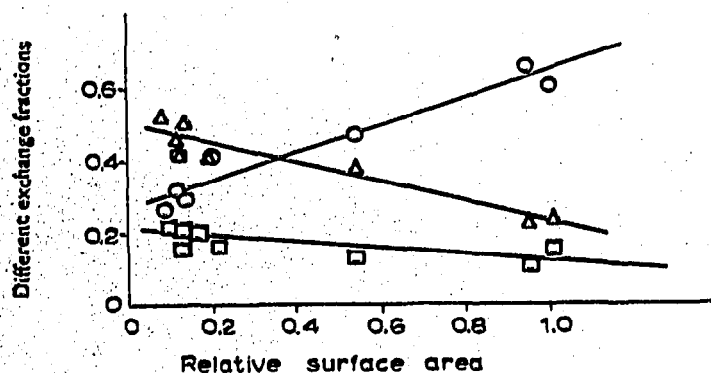


Fig. 3. Effects of relative surface area on F_I , F_{II} and F_{III} . \circ , F_I ; Δ , F_{II} ; \square , F_{III} .

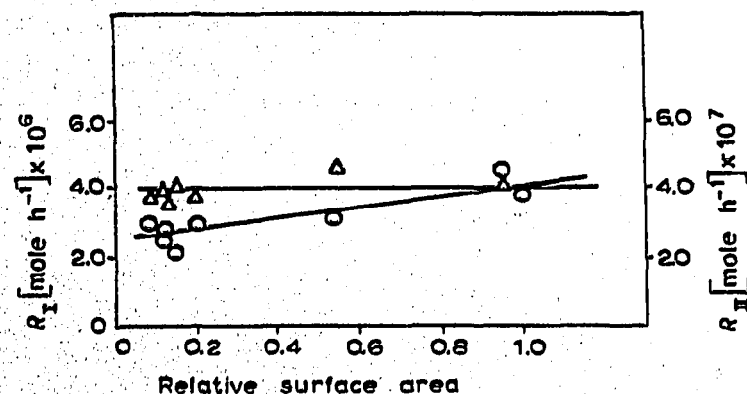


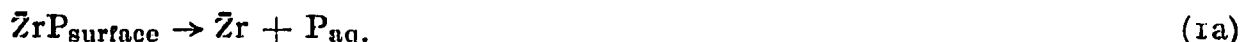
Fig. 4. Effects of relative surface area on reaction rates. \circ , R_I ; Δ , R_{II} .

Figs. 3 and 4 show the effects of relative surface area and indicate that the fastest process involves the phosphate groups at the surface of the solid. The independence of R_{II} (and R_{III}) upon surface area indicates that these processes are concerned with the reactions that occur in the interior of the solid particles. The observations that F_{II} and F_{III} decrease with increasing surface area are in accordance with the parallel increase of F_I , as $F_I = 1 - (F_{II} + F_{III})$.

It is convenient at this stage to put forward some hypotheses concerning the

nature of these processes. Process I, which is concerned with the reaction of phosphate groups at the surface of the material, may occur by one of the several mechanisms.

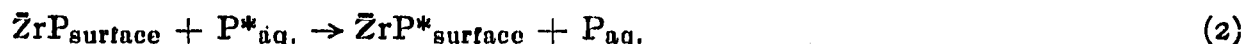
(i) The rate-determining step may be a dissociative process that can be written as



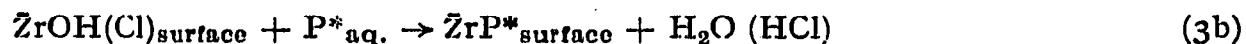
where $\bar{Z}r$ represents zirconium phosphate excluding the phosphate groups that are taking part in the reaction and P represents any one of the species PO_4^{3-} , HPO_4^{2-} , $H_2PO_4^-$ or H_3PO_4 and P^* denotes the same species labelled with ^{32}P isotope. The exchange would be completed by the reaction



(ii) A second possible mechanism of the reaction involving the surface of the solid may be a bimolecular reaction in which the entry of a labelled phosphate group into the solid is accompanied by the simultaneous release of a phosphate group from the solid. This reaction can be represented by the equation

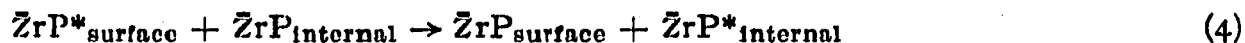


(iii) A third possible mechanism involves the hydrolysis of the phosphate groups at the surface. The reaction may be written as



Cl and HCl within parentheses indicate "acid hydrolysis", which may be possible under certain conditions²². The rate-determining step may be either reaction (3a) or (3b).

If, as seems probable, the slower process II represents a chemical reaction within the matrix of the material, then there may be possible reactions parallel to those for the faster process I. These can be viewed by replacing the suffix "surface" by "internal" for the above reactions. A fourth possible mechanism, which is absent for process I, is the isomorphous replacement of the phosphate groups at the surface by the internal phosphate groups and *vice versa*. This reaction may be written as



To decide between the various possible mechanisms postulated for processes I and II, it is necessary to discuss the effects of concentration upon the rates and equilibria of the exchange reactions.

It is shown in Fig. 5 that R_I as well as R_{II} increases with increasing solution concentration. This observation excludes the proposed mechanism given by reactions 1a and 1b. If reaction 1a is the rate-controlling step, then the reaction rate should be independent of the solution concentration, which is found not to be so. A dependence of the rate upon solution concentration could be expected for this mechanism

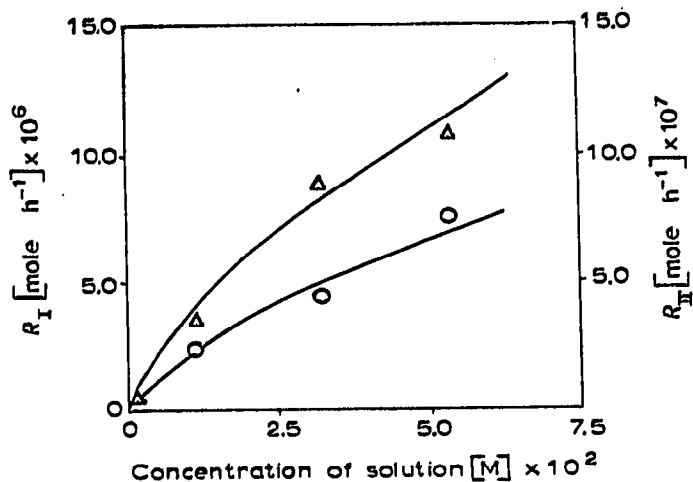


Fig. 5. Effects of concentration of solution on reaction rates. \circ , R_I ; \triangle , R_{II} .

only if reaction 1b were slower than 1a and therefore rate-controlling. This is very unlikely as reaction 1a involves bond cleavage and reaction 1b involves the formation of a zirconium phosphate linkage. A dependence of R_I and R_{II} upon the aqueous phosphate concentration would be expected for reaction 2 and also for the third mechanism if reaction 3b were rate-controlling. The kinetic observations of the direct exchange reactions are not able to distinguish between reactions 2 and 3a plus 3b as the mechanisms of the processes I and II. The mechanism for process II given by reaction 4 can be excluded because this mechanism suggests R_{II} to be independent of solution concentration.

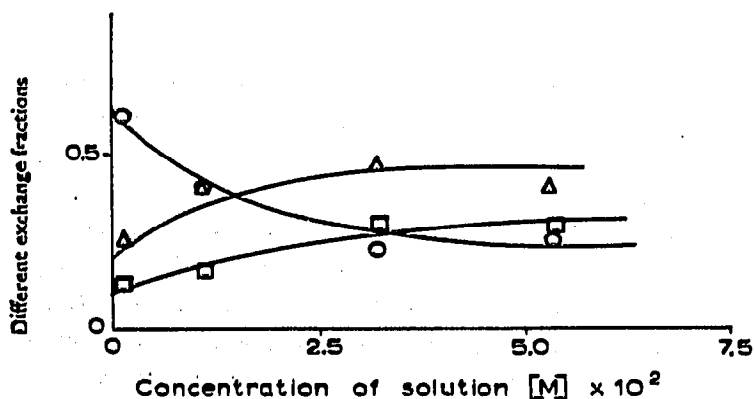


Fig. 6. Effects of concentration of solution on F_I , F_{II} and F_{III} . \circ , F_I ; \triangle , F_{II} ; \square , F_{III} .

It is shown in Fig. 6 that the extent of the equilibrium contribution by the process I, F_I , decreases while F_{II} and F_{III} increase with increasing concentration, levelling off at higher concentrations. From this observation, it seems that with increasing concentration some phosphate groups at the surface of the solid become unavailable for process I. In other words, with increasing solution concentration, the phosphate groups at the surface are converted to the phosphate groups related to other processes such as the internal process II or the internal process III, or both. If such interconversion occurs, it must do so at a rate that is considerably faster than

the rates of the exchange processes as pre-treatment of the solid with water or phosphoric acid solution does not affect the observed rates or F values.

It is possible that an increase in aqueous phosphate concentration causes blockage of the pores of the materials. In this way it is possible to envisage the conversion of surface-type groups to interior groups, which then exchange by either process II or III. It is also possible that by increasing the concentration of the phosphate groups in the aqueous phase, the extent of hydrolysis of the phosphate ions at the surface of the solid is suppressed, thus causing a decrease in the equilibrium contribution by process I. Such equilibrium control of the reaction may be the reason for the deviation from linearity of the curves in Fig. 5. Further evidence for the exchange reaction being equilibrium-controlled comes from the observation that R_I is approximately ten times higher than R_{II} . If the exchange were kinetically controlled and processes I and II were competitive, then it would be expected that F_I under all conditions would be considerably greater than F_{II} and would have a value of about 0.9. This has been demonstrated not to be so and kinetic control is therefore eliminated.

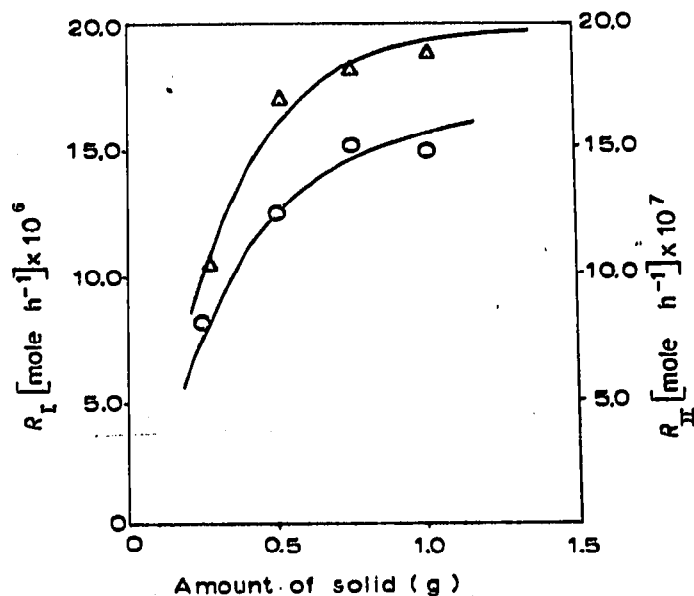


Fig. 7. Effects of the amount of solid on reaction rates. O, R_I ; Δ , R_{II} .

Fig. 7 shows that the rates R_I and R_{II} increase with the amount of solid. The increase in the rate with the amount of solid is expected for the proposed mechanism given by reactions 1a and 1b if reaction 1a were rate-controlling, which is likely to be so for the reason outlined earlier. The observed increase in R_I and R_{II} with increasing solid amount is in agreement with the proposed mechanism given by the bimolecular reaction 2. This observation is also expected for the mechanism given by reaction 4 for process II. If reaction 3b is rate-controlling, then the mechanism given by reactions 3a and 3b is consistent with the experimental observation of the increase in R_I and R_{II} with increasing amount of solid. This is understandable because the equilibrium hydrolysis producing $\bar{\text{ZrOH}}(\text{Cl})_{\text{surface}}$ is likely to increase with increasing amount of solid in contact with a fixed volume of the aqueous phase. In fact, VESELEY AND PEKAREK²³ have observed that the equilibrium phosphate release due to hydrol-

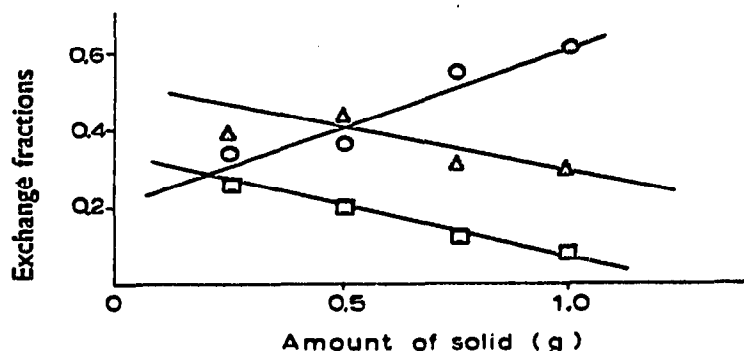


Fig. 8. Effects of the amount of solid on the exchange fraction. ○, F_I ; △, F_{II} ; □, F_{III} .

ysis increases with increasing weighed amount in contact with a constant volume of the aqueous solution of constant pH.

Fig. 8 shows that F_I increases linearly while F_{II} and F_{III} decrease linearly with the amount of the solid phosphate. If, as has been proposed earlier, there is a process in which surface-type groups are converted to interior-type groups, then an increase in the amount of solid will be equivalent to decreasing the solution concentration. In this way, the increase of F_I with increasing amount of phosphate in the solid phase can be interpreted in the manner discussed earlier for the effects of solution concentration. However, it should be noted that, except when changing the solution concentration from $1.1 \cdot 10^{-3} M$ to $1.1 \cdot 10^{-2} M$, the change in F_I with solution concentration from $1.1 \cdot 10^{-2} M$ to $5.3 \cdot 10^{-2} M$ is not sharp, but levels off in this range. It therefore seems that in addition to the probable blocking of the pores of solid particles, an increase in the amount of the solid selectively hydrolysed at the surface, causes F_I to increase. If this is the case, then the above observation agrees satisfactorily with the observation of VESELEY AND PEKAREK²³.

Based on the observed effects of the three variables discussed so far upon the rates R_I and R_{II} and the corresponding fractional contributions F_I and F_{II} for processes I and II, respectively, it is convenient to summarise the conclusions concerning the mechanisms of these processes. The observations are consistent with either reaction 2 or with reactions 3a and 3b, irrespective of whether or not the diffusion process is rate-controlling, while reaction 1 can be eliminated for process I and reaction 4 for process II. The mechanism given by reactions 1a and 1b is reasonably consistent for process II only if the diffusion process involved in reaction 1b is rate-controlling.

As with the slower process II, process III is concerned with the interior of the phosphate groups. Owing to the extremely slow rate of this process, R_{III} , it is very difficult to discuss the mechanism of process III. However, from the extremely slow rate observed, it seems that this process involves the internal phosphate groups, which are very strongly bound with the solid matrix. These phosphate groups may be engaged in crosslinking, assuming that the structure of the solid involves crosslinking. The exchange of these groups may involve de-crosslinking under favourable conditions followed by reactions similar to those of process II, the de-crosslinking being the rate-controlling step.

The study of the reverse exchange revealed further evidence for these three rate processes and also contributes to the knowledge of the detailed mechanisms of

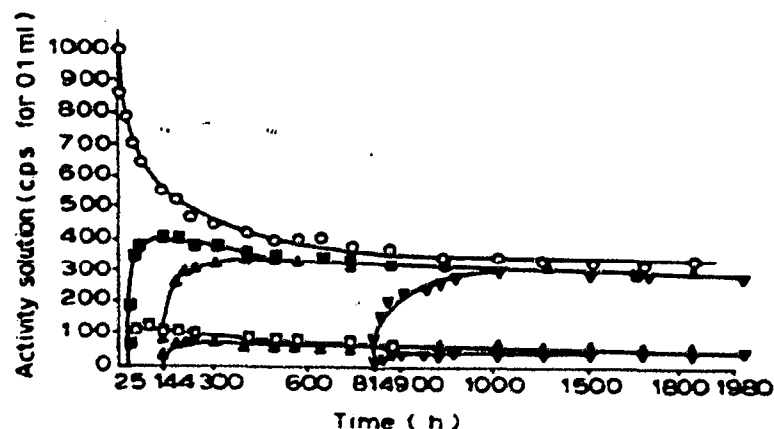


Fig. 9. Effects of labelling the solid to different extents. ○, ZrP + labelled H_3PO_4 ; ■, 29% labelled ZrP + H_3PO_4 ; □, 29% labelled ZrP + HCl; ▲, 58% labelled ZrP + H_3PO_4 ; △, 58% labelled ZrP + HCl; ▼, 82% labelled ZrP + H_3PO_4 ; ▽, 82% labelled ZrP + HCl. pH of acid = 1.1 in each case.

the processes. Fig. 9 shows that the activity release *versus* time plots have maxima. It appears that after some time the reaction is reversed and the activity is taken up instead of being released. Such results cannot be explained in terms of a single process.

From an analysis of the direct exchange reaction under the conditions of labelling, it could be calculated that of the 29% exchange, 24% had occurred by the faster process I and 5% by the slower process II. The corresponding values for 58% exchange are 41% and 17% by processes I and II, respectively. In the short time involved in this labelling, it was not possible to determine the extent of exchange by the third very slow process, which contributed to only negligible extent. If the direct reaction were allowed to go to completion, then the contributions to the exchange by the three processes were found to be 45%, 37% and 18% for F_I , F_{II} and F_{III} , respectively.

If the 18% of phosphate groups that are assigned to process III are discounted, then in the labelled material only $(5 \times 100)/(37)\% = 13.5\%$ and $(17 \times 100)/(37)\% = 46\%$ of the exchangeable internal groups were in fact labelled at the time of the start of the reverse reaction for the 29% and 58% labelled samples, respectively. This means that when the reaction was reversed, the isotopic equilibrium as far as process I was concerned, was in a state of imbalance in that the whole of the activity existed in the solid and none in the solution. After approximately 130 h (*ca.* $5 \times I_{t1}$), process I will have attained a state of isotopic equilibrium. During this time activity will be transferred from the solid to the solution phase by process I. Process II will not contribute to the transfer of the activity in the same direction. After a certain time, in which activity appears in solution, process II will contribute to the transfer of activity from the solution to the very much under-labelled solid. When the labelling of the internal phosphate groups is increased, process II will tend to be a two-way reaction in which some activity will be released into solution and some of the activity in the solution (which is mainly present because of process I) will enter the solid. Thus, the broadening and shifting of maxima with increased labelling can be explained. The experimental result can therefore be explained in terms of the two processes, one

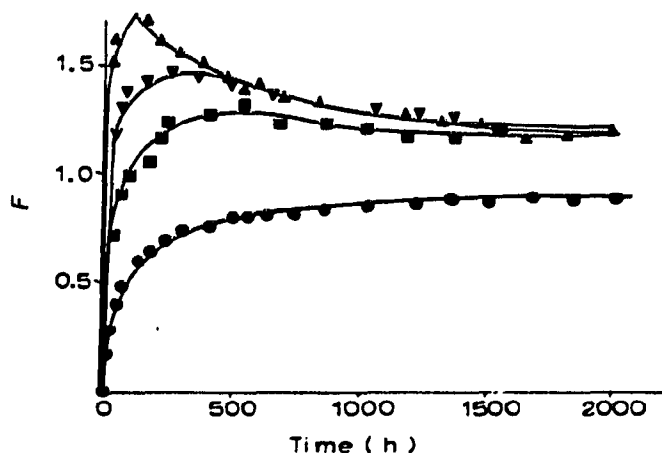


Fig. 10. Exchange fractions *versus* time for direct and reverse exchange. ●, $\text{ZrP} + \text{H}_3\text{P}^*\text{O}_4$ (direct exchange); ▲, $\text{ZrP}^* + \text{H}_3\text{PO}_4$ (reverse for 29% labelled solid); ▼, $\text{ZrP}^* + \text{H}_3\text{PO}_4$ (reverse for 58% labelled solid); ■, $\text{ZrP}^* + \text{H}_3\text{PO}_4$ (reverse for 82% labelled solid).

occurring rapidly on the surface of the material and the other occurring more slowly but generally in the reverse direction and accounting for the further exchange of the internal phosphate groups.

Corresponding to the maxima in the release of activity there are maxima in F values, which are more than unity, as shown in Fig. 10. This indicates that the solid phosphate labelled by the direct reaction is more than that involved in the reverse reactions. This may be due to the complexities that arise from the multi-directional flow of the activity, as discussed earlier. By mathematical treatment of a hypothetical reaction involving multi-directional flow of the activity, ABELL *et al.*²⁴ showed that the $(1 - F)$ *versus* time plot can have a minimum negative value, which is similar to the present observation.

It is likely that if solid zirconium phosphate is labelled to the extent of 100% or it is prepared using the ^{32}P isotope in the precipitant, thus ensuring the uniform distribution of the ^{32}P isotope throughout the solid phase, the plot of the exchange fraction F (calculated in the same way for both the reverse and direct reactions) *versus* time for the reverse reaction might coincide with that for the direct reaction.

In parallel to the reverse reactions, some hydrolysis reactions have been carried out. It has been shown in Fig. 9 that the activity release *versus* time plots for the solid in contact with an approximately 0.1 N solution of hydrochloric acid ($\text{pH} \approx 1.1$), in which the solid samples had been labelled to different extents by the direct exchange reaction, are of the same pattern as those for the reverse exchange reactions. The rate of labelling of the under-labelled solid during the hydrolysis reaction or the reverse exchange cannot be expected to be the same as that by the direct reaction because activity is flowing in two opposite directions. Hence, it was not possible to determine the exact amount of the solid that was labelled at any time during the hydrolysis or the reverse reaction. However, it is expected that towards the ends of such reactions, labelling of the solid samples, which were labelled to the different extents at the start, approaches the same isotopic equilibrium.

The fraction of the activity released to the total volume of the solution at any time of the hydrolysis reaction is not a true measure of the extent of over-all hydro-

ysis but of the hydrolysis of the fraction of the solid that is labelled at that particular time. Owing to the limitations of determining the exact extent of labelling, it is impossible to evaluate the exact extent of hydrolysis at any time during the hydrolysis reaction.

Towards the beginning of the hydrolysis reaction, activity is released to the solution by hydrolysis. When the amount of the activity released in this way exceeds the amount that would be present in the solution if there were uniform distribution of the activity throughout the system, then some activity is taken back from the solution by the under-labelled solid via the direct exchange reaction. As the extent of labelling of the solid increases, then for the hydrolysis reaction the maximum in the plot of activity release *versus* time is broadened and shifted to longer times after the start of the reaction.

If it is considered that after starting the hydrolysis reactions there was no more labelling of the solid, then the fraction of the activity released to the total volume of the solution, corresponding to the maximum value of released activity, would give the amount of the equilibrium hydrolysis of that fraction of the solid that had been labelled at the start of the hydrolysis reaction. If the increases in the extents of labelling between the start of the individual hydrolysis reactions and the time corresponding to the maximum value of released activity are discounted, then from Fig. 9 it is apparent that the rates and extents of hydrolysis of the 29% labelled fraction, 58% labelled fraction and 82% labelled fraction decrease in that order. This is due to the increased labelling of the internal phosphate groups. It is therefore clear that as with the exchange reaction, the hydrolysis reaction also consists of different steps, the rate and extent of hydrolysis of the surface groups being faster than those of the interior groups. This observation, together with the above arguments regarding the different steps of the hydrolysis reaction, suggests that reactions 3a and 3b are involved in processes I and II.

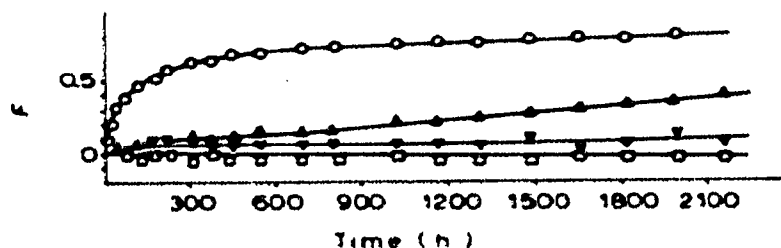


Fig. 11. Fractional exchange *versus* time for different conditions. \circ , ZrP (H⁺ form) + $3.2 \cdot 10^{-3}$ M H₂PO₄ of pH 1.1; Δ , ZrP (K⁺ form) + $3.2 \cdot 10^{-3}$ M H₂PO₄ of pH 1.1; ∇ , ZrP (K⁺ form) + $3.2 \cdot 10^{-3}$ M KH₂PO₄ of pH 1.1; \square , ZrP (K⁺ form) + $3.2 \cdot 10^{-3}$ M KH₂PO₄ of pH 4.4.

When the potassium form was used with phosphoric acid solution of pH 1.1, the *F* values were much lower than the corresponding *F* values for the hydrogen form of the samples, as shown in Fig. 11. If zinc phosphate had any cation-exchange properties, then the results observed by IONESCU *et al.*² might have the same cause. In their studies of the exchange of the phosphate ion between solid zinc phosphate and alkali phosphate solution, they observed that the rate as well as the extent of the exchange increased when alkali phosphate solution was replaced by a mixed solution of alkali phosphate and phosphoric acid.

When zirconium phosphate samples in the potassium form were allowed to

exchange with KH_2PO_4 solution of $\text{pH} = 1.1$, slight exchange occurred, as shown in Fig. 11. At such a pH it is likely that there was some conversion of the potassium form into the hydrogen form. It is further shown that when the zirconium phosphate samples in the potassium form were allowed to exchange with KH_2PO_4 solution of pH 4.4, the exchange was negligible. At such a pH there was no possibility of the conversion of the potassium form into the hydrogen form. This is a clear indication that the replacement of the exchangeable hydrogen ions by the potassium ions excludes the exchange of the phosphate ions.

PATERSON²⁰ has observed that the extent of hydrolysis is suppressed by a factor of about fifty when zirconium phosphate is in the potassium form and is kept in contact with potassium ions. This is a correlation between hydrolysis and the exchange of the phosphate ions, which suggests that the mechanism of the exchange reaction involving hydrolysis as shown in reaction 3a and 3b is the most probable one and that reaction 3b is rate-controlling for both processes I and II. Hydrolysis is the precursor for both processes. The diffusion of the phosphate groups within the matrix may be responsible for the slower internal process.

It is not clear whether the presence of the potassium ions or the accompanying crystallinity of the solid, or both, are the causes of the extremely limited hydrolysis and exchange capability of the solid. It would be useful to investigate the hydrolysis and exchange of crystalline zirconium phosphate in the hydrogen form.

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