

Hydrogen Exchange Studies and Proton Transfer in β Iron(III) Oxyhydroxide

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Dedicated to Professor Walter Feitknecht

Summary

The kinetics of hydrogen exchange between tritiated water and β -FeOOH crystals have been found to be dependent on pH in the alkaline region but independent in the acid region. The exchange formally obeyed a diffusion controlled law, and yielded the same activation energy 97 joules mole⁻¹ (23 kcal mole⁻¹) in both the alkaline and acid regions. The difference in kinetic behaviour on increasing pH in the alkaline region was attributed to a decrease in D_0 , the pre-exponential factor in the self-diffusion coefficient.

Pore size and surface area have been investigated in the characteristic cigarshaped crystals of β -FeOOH by means of

nitrogen isotherms. The pore size distribution calculated from the multilayer region of the isotherm was found to be very narrow and gave a mean pore diameter of 28.4 Å with a standard deviation of 7.0 Å. This agrees with the value of 30 Å found by WATSON *et al.*¹ using electron microscopy. Infra red data indicate weak hydrogen bonds of length 2.86 Å.

The implication of the weak hydrogen bonds, the orthogonal array of the large parallel channels, and the small structural tunnels, are considered in relation to possible mechanisms for hydrogen exchange.

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¹ J. H. L. WATSON, R. R. CARDELL and W. HELLER, *J. Physic. Chem.* 66 (1962) 1757.

Introduction

BÖHM^{2,3,4} discovered in 1925 that digestion of a hot solution of iron (III) chloride precipitated a new form of iron (III) oxyhydroxide which he called the β -form. Its crystal structure has been shown by MACKAY⁵ to be analogous to that of α -MnO₂ or hollandite⁶ with OH⁻ ions replacing half of the O²⁻ ions. The structure is thus an open one containing one tunnel per unit cell. These tunnels are square in cross section of side 3.4 Å. They are bounded by sides of 2 rows of fused octahedra and therefore belong to the class of 2 × 2 tunnels among oxide structures. They will hereafter be referred to as "structural tunnels". When first precipitated these are filled with Cl⁻ ions which are readily replaced by water molecules on washing with simultaneous conversion of OH⁻ to O⁻ to maintain electrical neutrality. According to MACKAY the trapping of large ions is necessary for the formation of the β -structure, this being achieved in the case of α -MnO₂ by the incorporation of Ba²⁺ ions.

Perhaps the most unique feature of β -FeOOH is that it forms tactoid colloidal crystals. FEITKNECHT has studied β -FeOOH over a number of years especially its formation in basic iron salt systems. He noticed that the spindle shaped crystals of β -FeOOH appeared to be built up from parallel oriented needles⁷. MACKAY⁸ observed parallel channels but detailed investigations of WATSON and CARDELL¹ following earlier work by ZOCHER and HELLER⁹ showed that the tapered or cigar-shaped crystals consisted of rod-like sub-crystals packed into an orthogonal array. These rods were 60 Å square in cross-section and up to 5000 Å in length, and when assembled into a regular parallel bundle, produced crystals ~600 Å wide, with tapered ends and of similar length. Evidence suggested that these rods were hollow the internal diameter being about 30 Å. They noted that the orthogonally packed array of sub-crystals is similar to the structure of liquid crystals of the nematic type. On standing for long periods in the solution from which they were precipitated, these crystals pack into regular layers called tactoids or Schiller layers which have the appearance of rafts, and correspond to the smectic phase in liquid crystals. They easily fall apart due to poor coherence, so that under the electron microscope both isolated and randomly oriented single crystals and rafts may be seen together. The sub-crystals cohere so well in the "nematic structure" of the spindle-shaped crystals that they only appear occasionally, having the appearance of long hollow tubes. Such rods offer the best visual evidence of

the hollow structure although micro-tome cross-sections of the single crystals show variations in intensity which are compatible with a packed array of hollow rods.

The primary object of this work was to investigate the exchange of tritium between liquid water and β -FeOOH crystals for comparison with other forms of ferric oxyhydroxide i.e. α -FeOOH and γ -FeOOH, which exhibit fairly strong but different arrangements of hydrogen bonded networks. The OH groups in β -FeOOH are on the other hand free or only very weakly hydrogen bonded. The results of previous studies^{10,11} suggest mechanisms in which the rupture of hydrogen bonds to form a defect water molecule is the rate determining step, the proton transfer within the hydrogen bond being relatively easy. It was imperative for the interpretation of the kinetics of hydrogen exchange in β -FeOOH that WATSON's proposed structure of packed hollow rods should be verified by another method and so the pore size distribution in β -FeOOH was determined by an N₂ adsorption-desorption isotherm at -196°C.

Experimental and Results

Preparation

Samples were prepared¹² by the hydrolysis of 4 litres of freshly prepared 0.1-M FeCl₃ solution at 80°. The precipitate was washed twelve times with 12 litre portions of distilled water by decantation. Peptization often occurred and this was removed by adding very small amounts of 2-M ammonia solution to the wash water. After drying at 110° the chloride content was determined and always found to be approximately 1 part per million by weight. The precipitates were not left long enough to develop tactoid crystals (i.e. Schiller layers) which require a minimum of two months at this concentration at room temperature. (See footnote 6 of Ref.¹.) This was confirmed by electron microscopy which showed only randomly oriented β -FeOOH crystals for which the mean width was 725 Å (standard deviation 62 Å) and the mean length 3500 Å. They had typically tapered ends.

Several batches were prepared but no differences in behaviour or characteristics outside experimental error could be observed in either X-ray diffraction, infra-red spectra, surface area measurements or kinetics of exchange.

X-ray diffraction

Powder photographs were taken on a Debye-Scherrer camera using iron filtered cobalt radiation. Values of 10 spacings were calculated and they agreed to within 1% of the values listed in the X-ray powder data file of the American Society for Testing Materials.

Infra-red spectra

These were used primarily to obtain more information on the hydrogen bonding in β -FeOOH. It is possible to estimate the hydrogen bond length in a crystal by the use of plots correlating OH-stretching frequency ν_2 with the O...O distance in oxygen-

² J. BÖHM, *Z. anorg. allg. Chem.* 149 (1925) 203.

³ J. BÖHM, *Kolloid-Z.* 42 (1927) 276.

⁴ J. BÖHM, *Z. Kristallogr.* 68 (1928) 567.

⁵ A. L. MACKAY, *Mineral. Mag.* 32 (1960) 545.

⁶ A. BYSTRÖM and A. M. BYSTRÖM, *Acta Crystallogr.* 3 (1950) 146.

⁷ W. FEITKNECHT, *Proceedings of the 4th International Symposium on Reactivity of Solids, 1960*, ed. DE BOER, Elsevier, Amsterdam 1961, p. 583.

⁸ A. L. MACKAY, *ibid.*, p. 579.

⁹ H. ZOCHER and W. HELLER, *Z. anorg. allg. Chem.* 186 (1930) 73, see also W. HELLER, *C. R. Acad. Sci.* 201 (1935) 831.

¹⁰ K. J. GALLAGHER and D. N. PHILLIPS, *Trans. Faraday Soc.* 64 (1968) 785.

¹¹ K. J. GALLAGHER and D. N. PHILLIPS, to be published.

¹² H. B. WEISER, W. O. MILLIGAN and E. L. COOK, *Inorganic Synthesis*, Vol. II, McGraw-Hill, New York 1964, p. 215.

oxygen hydrogen bonds. For hydroxyl compounds SCHWARZMANN has made this correlation on 17 compounds covering the range of hydrogen bond lengths of 2.6 to 3.8 Å and found a close fit to a single smooth curve¹³.

Infra-red spectra were taken routinely on each preparation but no data was available in the literature for comparison purposes. All samples were consistent and yielded the following values: OH stretching frequency, ν_2 3475 cm^{-1} ; OH bending frequencies, 1640 cm^{-1} and 1380 cm^{-1} . For 3475 cm^{-1} SCHWARZMANN's correlation plot predicts an O...O distance of 2.86 Å. The oxygen positions have not been determined by a full structure determination but we know from the periodicity along the c axis that one of the O...O distances is 3.02 Å and that the other short O...O distances are about 2.85 Å so that the hydrogen bond length from infra red is of the correct magnitude.

The OH stretching mode ν_2 had a high and narrow peak (half peak width 600 cm^{-1}) characteristic of free or weakly hydrogen bonded OH groups. The two bending frequencies were very weak.

Pore size and surface area determinations

A standard gas adsorption apparatus was used. Simultaneous pressure and volume measurements were made with an accuracy of ± 0.01 cm and ± 0.1 cm³ respectively. The desorption isotherm was measured after each adsorption isotherm. No hysteresis could be observed.

The surface area was calculated by the B.E.T. equation and found to be 30.7 ± 0.5 m²g⁻¹.

A pore volume distribution curve was determined for β -FeOOH by the method of BARRETT *et al.*¹⁴ which assumes that the pores are cylindrical and is shown in Fig. 1. The curve indicates a single narrow peak at 20 Å, but in order to determine the mean pore radius the volume distribution must be converted into a number distribution and a probability graph plotted.

If the pores are of equal length and cylindrical the number distribution of pores is given by the relation

$$\frac{\delta N}{\delta r} = \left(\frac{V_p}{\Delta r} \right) / (\pi \bar{r}_p^2 l), \quad (1)$$

where l = length of pore = length of crystal = 3500 Å,
 \bar{r}_p = mean pore radius in the interval Δr ,
 V_p = volume of pores in the interval Δr .

The number distribution was calculated by means of this equation and plotted in Fig. 1. The accumulative percentage of pores for each Δr was calculated. The 50% point yields a value of 28.4 Å for the mean pore diameter and the 16% and 84% points indicate a standard deviation of 7.0 Å (strictly the geometric standard deviation should be used for a log normal distribution but the distribution is so narrow that no significant error is introduced in using the more convenient standard deviation).

Tritium exchange between liquid water and β -FeOOH

Tritiated water of specific activity 7.0×10^5 counts sec⁻¹ per g atom of H was used throughout and tritium activities were measured as described previously¹⁰. The method of determining the exchange parameters have also been described in detail previously¹⁰ and consists essentially of exposing accurately weighed aliquots of about 0.1 g of β -FeOOH to 1 ml of tritiated water for different but increasing lengths of time

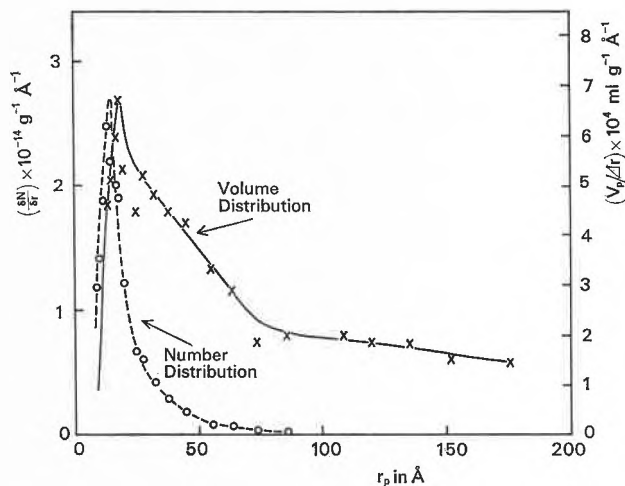


Fig. 1. The distribution of the volume ($V_p/\Delta r$) and the number ($\delta N/\delta r$) of pores against pore radius for β -FeOOH

in a thermostat controlled to $\pm 0.025^\circ$ until for the last aliquot, exchange is virtually complete. The tritium which had exchanged into each aliquot was measured from the water obtained by decomposing the β -FeOOH at 360° *in vacuo*. Each aliquot yields a point on the kinetic curve and a set of such aliquots was determined for a complete run.

The relative amounts of solid β -FeOOH and water used corresponds to a Berthier ratio of 0.01 which is sufficiently low to maintain the boundary conditions of constant activity C_1 at the solid surface, throughout the run. (The Berthier ratio is the ratio of exchangeable atoms in the solid and liquid phases.)

Runs were carried out at 26° for different pH values obtained by adding required amounts of HCl or NaOH and these are plotted in Fig. 2. Below pH 7 kinetic curves are indistinguishable but above pH 7 kinetic curves become progressively lower indicating slower exchange. The mechanism appears to be unaltered, however, as when plotted on a reduced time scale as in Fig. 3 all runs lie on the same curve.

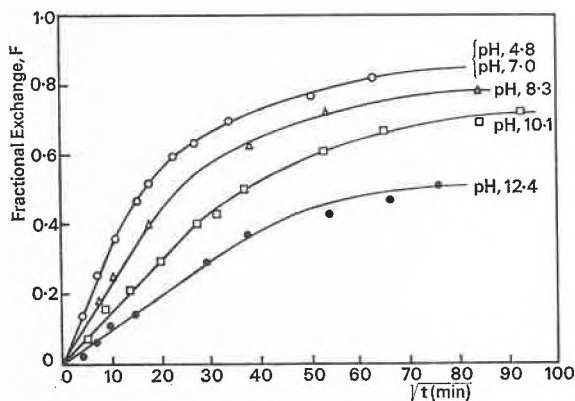


Fig. 2. Effect of pH on the kinetics of hydrogen exchange between β -FeOOH and liquid water. In this experiment tritium diffused from the liquid phase into the solid. Sample 4; temperature 26°C . $F = Q_t/Q_\infty$ where Q_∞ is the activity of the sample after infinity time

¹³ E. SCHWARZMANN, *Z. anorg. Chem.* 317 (1962) 176.

¹⁴ E. P. BARRETT, L. G. JOYNER and P. P. HALENDA, *J. Amer. Chem. Soc.* 73 (1951) 373.

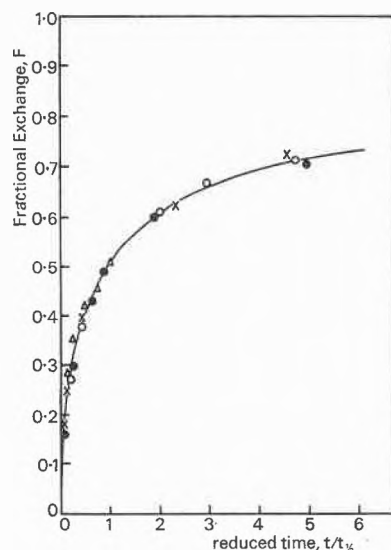


Fig. 3. As for Fig. 2 but on a reduced time scale $t/t_{1/2}$. \circ pH 4.8 and 7.0; \times pH 8.3; \bullet pH 10.1; \triangle pH 12.4. $t_{1/2}$ is the time required for half exchange

Up to a fractional exchange, F , of 0.4 the exchange obeys the equation for diffusion into a semi-infinite solid¹⁵

$$q_t = 2 C_1 \sqrt{(Dt/\pi)} = m \sqrt{t} \quad (2)$$

for the following boundary conditions; zero initial concentration in the solid, constant activity C_1 at the surface of the solid; and constant diffusion coefficient, D , where q_t is the activity taken up per unit area of solid surface after time t . For the whole sample

$$Q_t = 2 C_1 A (D/\pi) \cdot \sqrt{t} = m' \sqrt{t}, \quad (3)$$

Table I. Diffusion parameters of the exchange of hydrogen between β -FeOOH and liquid water

pH	Sample No.	T °K	m' sec ⁻¹ g ⁻¹	E activation energy for diffusion, joules mole ⁻¹
7.0	2	273.0	775.	99.9
		283.0	1210.	
		289.0	2479.	
		293.0	3616.	
7.0	5*	298.0	30.9	97.4
		308.0	58.3	
		318.0	107.5	
10.1	5	295.0	1128.	96.6
		303.5	1840.	
		308.0	2583.	
		314.5	3605.	

* In this run tritium exchanged out of the solid. See text for details.

¹⁵ J. CRANK, *The Mathematics of Diffusion*, Oxford University Press, London 1956, p. 31.

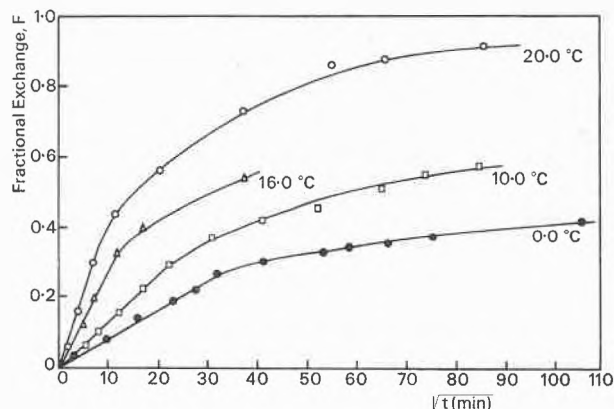


Fig. 4. Kinetics of hydrogen exchange between tritiated water and somatoids of β -FeOOH, at various temperatures. Sample 2, pH 7.0. Linear portion indicates that equation (3) is obeyed (tritium diffused into the solid)

where A is the surface area and Q_t the activity of the whole sample after time t . Since

$$D = D_0 \exp(E/RT).$$

E and D_0 can be determined as described previously¹⁰. These were obtained at two different pH values, and the results are shown in Table 1. A sample set of curves at pH 7 for different temperature is shown in Fig. 4. In some runs the pH of the water in contact with the last aliquot was measured and in all cases found to be the same as the initial value.

The kinetics of tritium exchange *out*, instead of exchange *in* was measured on sample 5. A portion of sample 5 was taken and tritiated to equilibrium by exposing at elevated temperatures to tritiated water of the same specific activity as that used for the runs with exchange *in*, until exchange was complete. The exchange was followed by measuring the activity of the liquid phase with time. The same amounts of solid and water were used and so the Berthier ratio was as before. In exploratory studies it was observed that the activity of the liquid phase after a given time was lower when shaken intermittently than when shaken continuously whereas for exchange *in*, no such differences were observed. For this reason samples during all runs were shaken continuously. The results of the exchange *out* on sample 5 are shown in Table (indicated by 5*).

Discussion

WATSON *et al.*¹ and MACKAY¹⁶ have drawn attention to the possibility that β -FeOOH does not form normal homogeneous crystals. The crystals have tapered or irregular ends. Single crystals of irregular external shape were noted by KOHLSCHÜTTER¹⁷ who put them into a distinct class of their own which he called *Somatoids*.

¹⁶ A. L. MACKAY, *J. Physic. Soc. Japan* 17 (1962) 317.

¹⁷ V. KOHLSCHÜTTER, C. EGG and M. BOBTELSKY, *Helv. Chim. Acta* 8 (1925) 457.

The regularly packed array of hollow tubes proposed WATSON *et al.*¹ have an important bearing on the study and interpretation of the kinetics of exchange and so it was imperative to check the existence of such pores and also their dimensions. This was most simply done by pore volume determinations from the N₂ adsorption isotherm. The mean pore diameter thus determined (28.4 Å) agrees well with the value of 30 Å of WATSON *et al.* For the exchange work it is necessary to know the atomic structure of the walls of the tube. From unit cell dimensions and the hollandite structure an atomic model for the tube has been suggested¹⁸. In this model the walls of the tube are one unit cell thick and the cross-sectional area of the large pore is 885.6 cm² which may be compared with the value of 748 cm² calculated for a cylindrical pore of diameter 28.4 Å. The difference, 138 cm², corresponds to the cross-sectional area of a layer of water on the inner surface of the pore, which would probably remain even after the drying process.

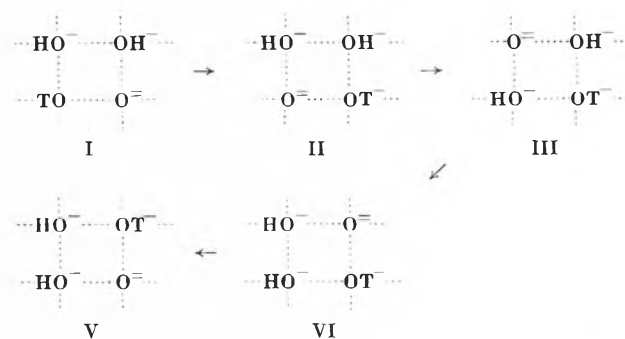
The structural tunnels, on the other hand, would have a different influence on the kinetics. According to MACKAY⁵ Cl⁻ is replaced by water molecules and our TGA studies indicate that β-FeOOH has excess water according to the formula FeOOH · ¼(H₂O) which corresponds to one H₂O molecule in every Ba position in the hollandite structure. (The formula of hollandite is Ba□Mn₈O₁₆ where the Ba atoms is randomly distributed over twice their number of sites in the tunnels; □ represents a vacant site.) Hence the washing process may be expressed thus, FeO_{1-¼} · (OH)_{1+¼} · ¼Cl → FeOOH · ¼(H₂O). Our TGA studies indicate that this water would remain in the crystal during the drying process as well as during exchange.

Before considering the part this water might play in the exchange process, its environment in the tunnel and the effect this may have on the state of the water molecules must be examined closely. Since these H₂O molecules occupy the original Cl sites (i.e. Ba sites of the hollandite structure) they will be only 2.84 Å away from nearest oxygens to which they will be at least weakly hydrogen bonded. Indeed the strength of such hydrogen bonds will be very similar to those existing between nearest oxygens in the rest of the β-FeOOH structure and which are also about 2.84 Å apart. On the average some of these will be oxide ions (O⁻). Since these are very strong proton acceptors, it is unlikely that H₂O will remain undissociated in this environment and will almost certainly lose a proton to a nearby oxide ion, forming two OH⁻ ions, one of which will occupy the Cl position. If the formula is written Fe₄O₉H₆ it will be seen that such a dissociation will increase the ratio of oxide to hydroxide ion from ½ to ⅓, and the net effect is equivalent to replacing Cl⁻ in FeO_{1-¼} · (OH)_{1+¼} · ¼Cl by OH⁻ ions instead of water molecules. It would be interesting to check this prediction, based on the LOWRY-BRÖNSTED theory of acid-base behaviour, by neutron diffraction studies.

The activation energy for tritium exchange between β-FeOOH and water is considerably higher than for α-FeOOH (34.3 joules mole⁻¹)¹⁰ and γ-FeOOH (58.7 joules mole⁻¹)¹¹. The shortest hydrogen bond length in β-FeOOH is 2.85 Å* which is longer than the hydrogen bonds in ice and water (2.76 Å). Such a long bond indicates a very weak interaction or nearly free OH groups. An approximate value of the hydrogen bond energy may be obtained from the correlation plot of LIPPINCOTT and SCHROEDER¹⁹ which indicates that hydrogen bonds of 2.85 Å have energies of about 12.5 joules mole⁻¹ (3.0 kcal mole⁻¹). Thus the breaking of hydrogen bonds will not be the rate determining step for the diffusion of tritium. Without strong or moderately strong hydrogen bonds, however, the potential energy barrier for proton transfer from one oxygen to another, of the kind proposed¹⁰ in the mechanism for proton transfer in α-FeOOH, will be very high; higher than even for water and ice. The value for water is given by the heat of neutralization of an acid and a base which is 56.4 joules mole⁻¹ (13.5 kcal mole⁻¹) at 25 °C²⁰. Thus the activation energy for hydrogen bonds longer than 2.76 Å must be higher than 56.4 joules mole⁻¹ and is probably considerably higher.

Above a value of 7, increasing pH causes a progressive decrease in exchange rate. D₀ but not E is affected. This suggests that although the mechanism is the same, H₃O⁺ plays an important role. What is surprising, however, is that the diffusion process within the solid is affected by the pH of the liquid phase. A possible explanation of this behaviour is discussed below.

There are two possibilities for the proton exchange in β-FeOOH. The first possibility arises from the ability of an assembly of O⁻ and OH⁻ ions weakly hydrogen bonded to one another, to allow a flow of protons through the solid by a simple mechanism which is illustrated below on a group of oxides and hydroxide ions.



* The atomic positions have not been determined experimentally. We have calculated this from the unit cell dimensions and the hollandite structure based on perfect octahedral coordination of Fe by oxygens.

¹⁸ K. J. GALLAGHER, to be published.

¹⁹ E. R. LIPPINCOTT and R. SCHROEDER, *J. Chem. Physics* 23 (1955) 1099.

²⁰ H. M. PAPEE, W. J. CANADY and K. J. LAIDLER, *Can. J. Chem.* 34 (1956) 677.

Each of these steps is a transfer of a proton or triton from an OH^- to an O^{2-} ion and requires $96 \text{ joules mole}^{-1}$ ($23 \text{ kcal mole}^{-1}$). This mechanism depends on OH^- ions rotating almost freely and thus there is no need to postulate defect water molecules as in $\alpha\text{-FeOOH}$, because there are no strong hydrogen bonds, nor as in $\gamma\text{-FeOOH}$ because oxide and hydroxide ion sites are interchangeable.

The second possible mechanism arises from the parallel bundle of tubes whose large (30 \AA) pores make the whole of the interior of the solid accessible to the liquid phase when immersed in tritiated water. One would not, on the whole, expect water molecules to be very mobile in such pores, partly because these pores are very small and partly because the walls of the pores consist of ions some of which are triply charged (Fe^{3+}) and doubly charged (O^{2-}). Such high charges will promote an ice-like structure in the pores and may prevent the water acquiring a fully liquid condition even at the exchange temperatures. The degree of ice character will diminish with distance from the wall to the centre of the pore where it will be least. The number of concentric water layers in the pores will be approximately eight. Nevertheless we would expect the exchange to be similar both in mechanism and in the magnitude of the kinetic parameters with that in ice. The self-diffusion coefficient of deuterium in ice has been found by KUHN and THÜRKAUF²¹ to be equal in magnitude to that of ^{18}O in ice from which they concluded that exchange takes place by the diffusion of H_2O molecules and not by hydrogen atoms moving independently. Unfortunately activation energies and other kinetic parameters were not determined and so it is not possible to compare them.

Neither possibility excludes the other but if the second operates the first is needed to explain exchange between water in the pores and in the interior of the pore walls. The first mechanism, however, does not require the second even as a preliminary step, as triton could diffuse

along the interior of the walls from the outer surface, but the inclusion of the second mechanism as the initial stage is favoured by the remarkable influence of pH on the kinetics of exchange. For a non-porous solid pH could have no influence on the exchange unless surface processes, sensitive to pH , were rate determining. In a diffusion mechanism surface processes can only be rate-determining for some initial period when the diffusion rate is high. None of the runs indicated that the influence of pH ceased after an initial period and so such an explanation appears unsatisfactory. If, however, exchange took place *via* water in the pores instead of diffusion through the strictly solid phase then pH is likely to have an influence for the whole of the reaction. We have no knowledge what effect pH might have on the mechanism of proton exchange, as no measurement of tritium diffusion through water or ice at different pH values, have been made. Thus the mechanism for hydrogen exchange is at present unresolved and further studies are required.

It would appear that successive studies on $\beta\text{-FeOOH}$ continue to reveal properties markedly different from classical crystalline solids. One might expect yet more unique features especially as the result of the application of other techniques. The use of neutron diffraction is particularly likely to reveal new facts about this unique substance, especially about the position of the hydrogens both in $\beta\text{-FeOOH}$ itself and in the product after replacing Cl^- by H_2O molecules. The structure of $\beta\text{-FeOOH}$ is so clearly related to and dependent on the conditions of the starting materials that a detailed study of its formation in solution may have much to reveal about that relatively unexplored area, the process of precipitation of transitional metal oxides and hydroxides from solution.

Our thanks are due to Professor RHODES, formerly of this college, for the use of X-ray diffraction facilities and to Dr. STEDMAN for helpful discussions. One of us (D. N. P.) thanks the Thomas and Elizabeth Williams Fund for a studentship.

²¹ W. KUHN and M. THÜRKAUF, *Helv. Chim. Acta* 41 (1958) 938.