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HYDROGEN AND OXYGEN ISOTOPES APPLIED TO THE STUDY OF WATER-METAL REACTIONS. EXCHANGE OF D_2O^{18} WITH ALPHA ALUMINA MONOHYDRATE

by

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ABSTRACT

Isotopes of hydrogen and oxygen may be useful in elucidating the mechanism of aqueous corrosion reactions, in which an important step may be diffusion of protons and/or hydroxyl (or oxide) ions through a thin protective film. The technique of isotope exchange and the kinetic isotope effect both appear applicable.

For the reaction between water and aluminum, the product (above 90°C) is α-alumina monohydrate (α-AlOOH). The exchange of D_2O^{18} with α-AlOOH (sub-micron crystallite size) was examined from 100 to 230°C. The rate of D-H exchange was appreciable; O^{18} exchange was slow. The O^{18} content of the separate phases suggested that only half the O atoms in α-AlOOH are exchangeable.

Results were interpreted on the basis of a slow step involving independent diffusion of protons and oxygen carrier ions. The activation energy for the proton diffusion coefficient was ~12 kcal.

The isotope exchange technique was applied to the reaction between water and aluminum at 100°C. Al (type 1100) sheets reacted with H_2O to the "protective film" stage, then with D_2O. The D content of the film increased, but the net exchange (corrected for D uptake) was only slight. Impurities (Fe and Si) in the Al may enter into the α-AlOOH lattice and reduce proton mobility.

Further corrosion-exchange studies with pure aluminum are needed to decide whether or not there exists a relationship between proton lability and corrosion rate. The D isotope effect on the rate of aqueous corrosion reactions should be useful in assessing the importance of proton mobility in the mechanism.

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INTRODUCTION

Hydrogen and oxygen isotopes may be useful in elucidating the mechanism of aqueous corrosion reactions. The principal isotopic techniques which may be employed are the isotopic exchange method and the kinetic isotope effect.

An important step in a number of postulated mechanisms of corrosion(1,2) involves the diffusion of hydrogen and/or hydroxyl (or oxide) ions through a thin protective "barrier film" of oxide (or hydrated oxide). The question of the lability of the oxygen and/or hydrogen in the film may be answered by measuring the rate of exchange of isotopically labelled water containing O^{18} (or O^{17}) and deuterium (or tritium) with the isotopically normal corrosion product, either as a stripped film or present as a growing film on the metal. Quantitative measurements of the isotope exchange rate may be used to evaluate the diffusion coefficient of the labile species in the corrosion product, provided that the dimensions of the solid particles involved are known. Even semi-quantitative measurements may be sufficient to yield information on the relative lability of protons or oxygen carrier (e.g., hydroxyl) ions in the film.

The kinetic isotope effect involves measurement of the relative rates of reaction of various isotopic water molecules with the metal. The magnitude of the deuterium or tritium isotope effect may be used to distinguish qualitatively among three rate-determining steps. A "large" isotope effect ($k_H/k_D \cong 5$) with an appreciable temperature coefficient is generally associated with a process involving a rupture of a bond, such as the oxygen-hydrogen bond. Johnston and Davis(3) studied the initial relative rates of reaction of H_2O and HDO with various metals at 30°C. The first fraction of hydrogen evolved was always depleted in deuterium. For the dissolution of aluminum in H_2SO_4 and in NaOH, the isotopic fractionation factor was 4.5 and 5.0, respectively. A "moderate" isotope effect($k_H/k_D \cong 1.5$), with only slight temperature coefficient, is associated with a duffusion process, e.g., protons <u>vs</u> deuterons. A negligible hydrogen isotope effect would imply that the rate-determining step was neither bond rupture involving hydrogen nor proton mobility through a film.

For the oxygen isotope effect, both measurements and interpretation are more subtle. The magnitude of the effect is small (<u>ca.</u> 1-3%) and the temperature coefficient difficult to determine. Competitive measurements involving the isotopic fractionation technique are required.

Very little previous data on the application of hydrogen and oxygen isotopes to the water-metal reactions are available in the literature. Feitknecht and Zbinden(4) mention the exchange of D_2O with $Mg(OH)_2$ crystals. Winter(5) has studied O^{18} exchange between oxygen and a number of oxides at elevated temperatures.

The present report summarizes a preliminary study of the aluminum-water system at temperatures above 100°C, where it is known that the stable corrosion product is α-alumina monohydrate (α-AlOOH or boehmite). Below 90°C, β-alumina trihydrate (bayerite or $Al(OH)_3$) is the stable product.

The isotope exchange reaction between liquid D_2O^{18} and crystalline α-AlOOH (of sub-micron particle size) was investigated from 100 to 230°C. A cursory study of the exchange with bayerite was also made. In addition, an attempt to measure the exchange of deuterium between water and the growing corrosion film on aluminum (type 1100) was made. This type of "corrosion-exchange" experiment may have applicability to other systems.

Preliminary results by Mori and Draley(6) on the relative rates of reaction of Al (type 1100) with H_2O and D_2O at 100°C are discussed.

EXPERIMENTAL

A. Materials

D_2O^{18} (99.8 at.% D, 1.4 at.% O^{18}, Stuart Oxygen Co.) was used in most of the exchange studies. In a few cases D_2O^{16} (99.6 at.% D) was used.

1. Boehmite, α-Al_2O_3 monohydrate (Analysis:(7) % Al_2O_3: 84.95, 84.56, 84.69, 84.75; Calc. for AlO_2H: 84.98%) was prepared(8) by the reaction of high-purity aluminum (>99.99%) with H_2O at 350°C for approximately 15 hours. X-ray diffraction photographs(9) of samples from several different preparations revealed no lines due to crystalline impurities. A microphotographic investigation(10) of several batches indicated a particle size distribution with a maximum corresponding to a most probable diameter of 0.5μ. B.E.T. N_2 surface area measurements(11) gave a value of 12.2 m^2/g, corresponding to an effective particle diameter of approximately 0.16μ. Apparently a large number of fine particles ($d<0.1\mu$) were undetected in the micrographs.

2. Bayerite (β-Al_2O_3 trihydrate) was kindly supplied by Dr. R. Van Nordstrand, Sinclair Research Lab., Harvey, Ill. Analysis:(7) % Al_2O_3: 65.15; Calc. for AlO_3H_3: 65.35. X-ray diffraction photographs(9) showed no crystalline impurities. Particles were rod-like and larger than those of the boehmite.

B. D and O^{18} Analyses

In most cases water samples (ca. 25 mg) were assayed for D by infrared spectrophotometry.(12) A 2-mm quartz cell was used. A calibration curve using the bands at 1.64μ (HOD) and 1.44μ (HOH) was prepared.

The results were reliable to about ±1 at.% D. Smaller water samples (7-10 mg) were converted to hydrogen by reaction with zinc in sealed Pyrex 1720 tubes at 700°C for one hour.(13) The H_2-HD-D_2 mixtures were analyzed mass spectrometrically.(14)

Water samples were assayed for O^{18} by conversion to oxygen gas. Approximately 10-mg samples (contained in small gold cups) were reacted with BrF_3(15) and the evolved O_2 assayed for O^{18} mass spectrometrically.(14,16) Aluminum oxide samples were treated(17) with $KBrF_4$ at 500°C to liberate O_2 for O^{18} assay.

C. Infrared Spectra

Infrared spectra of crystalline samples were obtained(18) with Perkin-Elmer Model 21 Spectrophotometers (NaCl optics) and a Beckman IR4 Spectrophotometer (NaCl) using the KBr pellet technique (0.5-1 wt.% in KBr).

D. Procedures (Exchange Experiments)

Exchange experiments were performed under a number of different conditions. In most cases they were carried out with 1-2 g of α-AlOOH and greater than equimolar quantities of liquid D_2O^{18} in glass ampoules. In certain cases, the ampoules were de-gassed; in most cases ampoules were capped in air. For temperatures above 125°C, stainless steel hydrothermal bombs were used, both with and without glass liners. No marked differences attributable to the different ampoule procedures were noted.

For the rapid exchanges at room temperature (i.e., with bayerite) ampoules were mounted on a shaker. Otherwise, the ampoules were agitated periodically.

The extent of deuterium exchange was determined from the D assay of the solid and/or liquid phase. After centrifuging, the water was assayed for D and O^{18}. The solid phase was vacuum dried and then, after evacuation ($<10^{-4}$ mm Hg) at room temperature, subjected to dehydration at 400-500°C *in vacuo*. The water was collected and weighed. Generally 96-98% of the stoichiometric quantity of water was collected. X-ray diffraction(9) indicated that the residual crystalline solid was γ-alumina.

In a number of cases, the total oxygen was removed from the solid α-AlOOH by treatment with $KBrF_4$ at 500°C.(17) Oxygen yields of 97-99% of stoichiometric were obtained.

Experiments involving exchange of deuterium with a growing corrosion film were carried out as follows: eleven samples of aluminum sheet (type 1100; typical analysis: 99.2% Al, 0.52% Fe, 0.13% Si, 0.12% Cu.), each of total area approximately 200 cm^2, were prepared(8) by etching with HNO_3-HF solution and washing. They were allowed to react with boiling distilled water (ca 100°C) for a time (5-8 days) sufficient to reach the condition where the rate of weight gain decreased to an essentially constant (low) value.(19) Then the samples were exposed to D_2O at 100°C for varying periods of time, during which exchange of D with the slowly growing film was occurring. Weight gain measurements were made to enable estimation of a correction for D uptake in computing the percentage exchange. The sheets were stored after vacuum drying in a dessicator.(20)

The films were subjected to evacuation ($< 10^{-4}$ mm Hg) at room temperature, then dehydrated at 450-500°C in vacuo. The water was collected and weighed. In all cases, the weight of water collected was in good agreement with that calculated from the weight gain: for eleven similar samples the average weight of water recovered in the dehydration was 8.0_2 mg compared to that calculated, 8.0_1 mg, from the (average) weight gain. The average deviation for individual samples was ± 0.4 mg.

RESULTS

Figure 1 shows the rate of exchange of D_2O with boehmite at several temperatures from 25°C to 230°C. The percentage exchange is plotted vs the square root of the time. Because of the great dependence of the exchange rate on the particle size and the molar ratio of the liquid and solid phases (to be discussed later), these data have only semi-quantitative significance. They indicate that for sub-micron particle size α-AlOOH, the D exchange reaction proceeds fairly rapidly above 100°C.

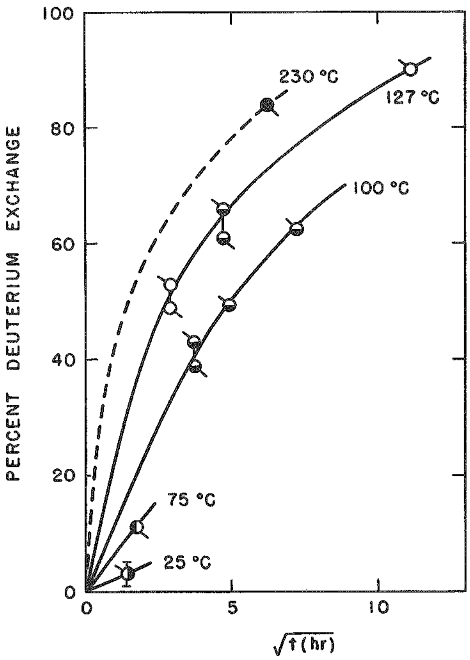

Fig. I. EXCHANGE OF D_2O WITH BOEHMITE (AlOOH) POWDER.
Percent exchange based on D assay of:
water Boehmite

Figure 2 shows the temperature dependence of the initial slopes (estimated from Figure 1) of percentage exchange vs $t^{1/2}$. From the slope of the graph of log (initial slope) vs 1/T, an "activation energy" of 5.8 ± 1.3 kcal/mole is estimated.

Figure 3 shows the rate of O^{18} exchange between D_2O^{18} and boehmite at 100°, 127° and 230°C. The apparently anomalous temperature dependence is probably not real. In any case, it is evident that the rate of exchange for O^{18} is appreciably less than that for deuterium.

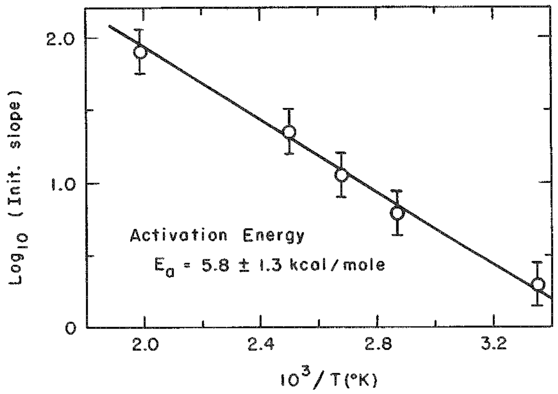

Fig. 2. TEMPERATURE DEPENDENCE OF INITIAL SLOPE IN THE RATE OF EXCHANGE OF D_2O WITH BOEHMITE (AlOOH) POWDER.

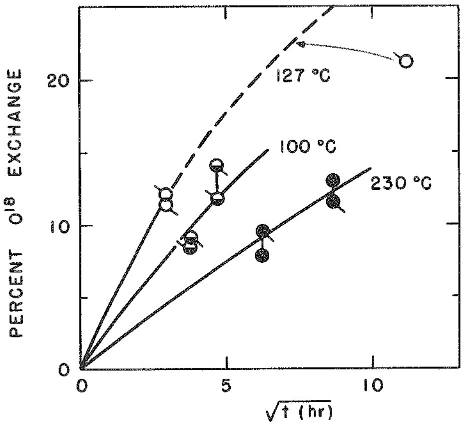

Fig. 3. EXCHANGE OF D_2O^{18} WITH BOEHMITE (AlOOH) POWDER. % exchange based on O^{18} assay of: ⊸ Water; ⊖ Dehydration water from Boehmite; ● Total O_2 from reaction of $KBrF_4$ with Boehmite, assuming ½ of O atoms in AlOOH exchangeable.

It was assumed in computing the per cent exchange of O^{18} that one-half of the O atoms in AlOOH were exchangeable. The data on the O^{18} content of the separate phases after exchange could not be reconciled without making this assumption. An unsuccessful attempt to obtain direct experimental confirmation of this was carried out by allowing an exchange between excess D_2O^{18} and boehmite to proceed for 27 days at 230°C. However, only 14% of the (total) O atoms in the AlOOH exchanged, corresponding to 28% of the (assumed) equilibrium value.

Figure 4 shows the results of a corrosion-exchange experiment at 100°C with eleven samples of type 1100 aluminum. The corrosion in H_2O after the first 164 hr produced an average weight gain of 13.9 mg/dm^2. The additional weight gains in D_2O ranged up to 1.15 mg/dm^2. The observed deuterium content of the boehmite film is corrected for the uptake of deuterium (known from the weight gain) to give the curve for the net exchange. The slight and nearly constant value (ca 5% exchange) may represent only surface exchange. Since the total boehmite film thickness is calculated to be of the order of 1 micron, it is surprising that such a small rate of exchange is observed. From Figure 1, at 100°C the half-time for

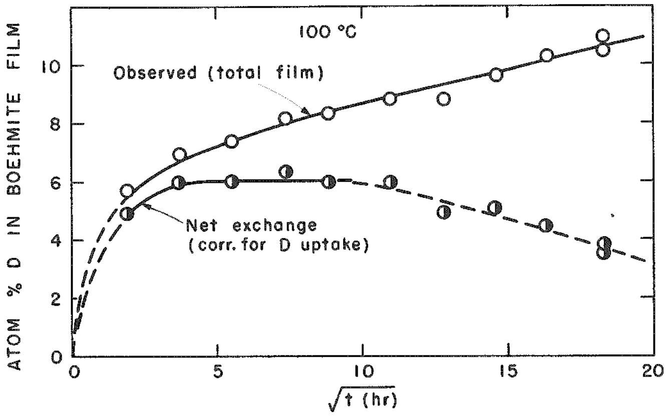

Fig. 4. EXCHANGE OF D_2O WITH BOEHMITE (AlOOH) FILM ON ALUMINUM (Type 1100). AlOOH FILM FORMED BY PRIOR EXPOSURE IN H_2O FOR 164 HOURS AT 100 °C, PRODUCING AN AVERAGE WEIGHT GAIN OF 13.9 mg/dm^2. WEIGHT GAIN IN D_2O RANGED UP TO 1.15 mg/dm^2.

○ Observed (total)

◑ Net exchange corr. for D uptake from weight gain data.

deuterium exchange is approximately 24 hr for the crystalline α-AlOOH of particle size comparable to this dimension.

A gross sample of boehmite prepared(8) from type 1100 aluminum was gray in color and contained(7) Fe and Si in the amounts anticipated from the analysis of the 1100 aluminum. It was hypothesized that the impurities may enter into the boehmite lattice in such a way as to reduce the mobility of the proton. To clarify this point, a number of exchange experiments were carried out with the impure boehmite at 100°C. It was found that deuterium exchange did occur, but at a reduced rate compared to pure α-AlOOH. Because of the uncertainty in particle size no valid quantitative comparison was possible; however, the impurity effect alone is insufficient to explain the unexpected low rate of exchange of D_2O with the corrosion film on 1100 aluminum at 100°C. Further corrosion-exchange experiments with pure (>99.99%) aluminum are required.

Figure 5 shows the exchange of D_2O with bayerite crystals at 25°C. In view of the fact that the particle size was much larger than that of the boehmite and that the exchange proceeds at convenient rates at room temperature, it is clear that the proton mobility in bayerite is at least an order of magnitude greater than in boehmite.

Figure 6 shows the infrared spectra of beohmite* and boehmite-d (approximately 90% deuterated). Table I lists the spectral data. The strong O-H stretching frequencies near 3000 cm^{-1} are seen to be shifted

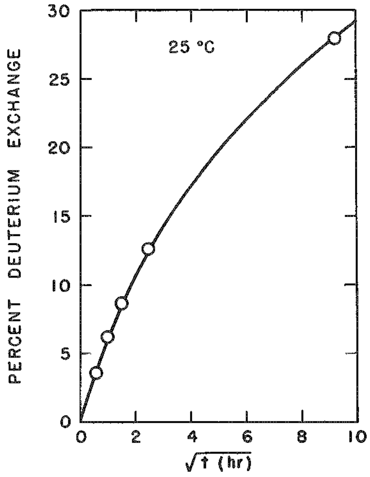

FIG. 5. EXCHANGE OF D_2O WITH BAYERITE ($Al_2O_3 \cdot 3H_2O$) POWDER (Sinclair).

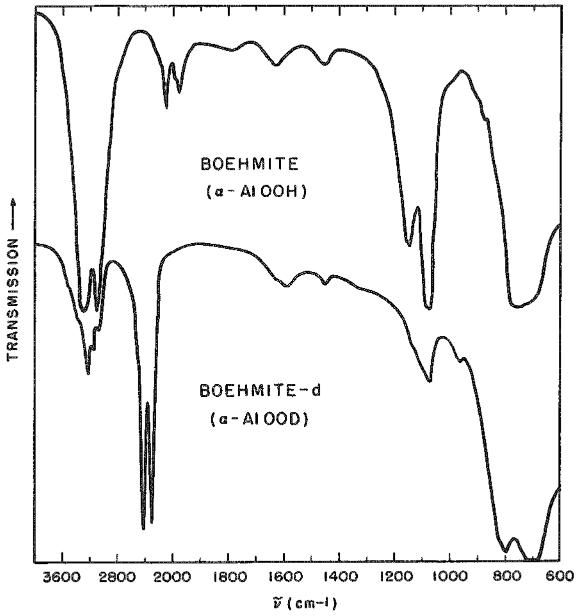

Fig. 6. INFRARED SPECTRA OF BOEHMITE AND BOEHMITE-d (ca 90% D) PELLETS, approx. ½% in KBr.

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*Note added in proof: The spectrum of boehmite is in good agreement with that reported by Shipko and Haag, KAPL-1740 (July 10, 1957); Unclassified Mar. 25, 1958.

down to the O-D region by the usual ratio (approximately 0.75). The (presumed) O-H-O bending frequencies near 1100 cm^{-1} also shift downward by a similar ratio. The "water of hydration" bands at 3500 and 1620 cm^{-1} are of only very low intensity in the spectrum of α-AlOOH and may be due to adsorbed moisture. This is similar to the case(21) of $HgOHNO_3$ (compared to $Hg(NO_3)_2 \cdot H_2O$), where the O-H stretching frequency is appreciably displaced relative to the O-H band in hydrate water and the hydrate band in the 1620 cm^{-1} region is absent. An interpretation of the O-H stretching frequency in terms of the hydrogen bond structure is given in the Discussion section.

Table I

INFRARED SPECTRAL DATA[a] FOR α-AlOOH AND α-AlOOD (90%D)

α-AlOOH	α-AlOOD (90%D)	Comments
695 vvs, b	720 vvs, b	
760 vvs, b		
	810 vvs	O-D-O bend
	975 w	
1085 vvs	1075 m	O-H-O bend
1155 s	-	
1460 w	1460 vvw	
	1580 w	
1630 w	1625 vvw, sh	hydrate water ($\cdot H_2O$)
1790 vw, b		
1970 w		
2120 m		
	2360 s	O-D stretching region
	2460 vs	
3120 vvs	3125 m, sh	O-H stretching region
	3200 s	
3310 vvs, b	3290 s	
	3450 m, sh	

[a] Expressed in wavenumbers (cm^{-1}), s = strong, m = medium, w = weak, v = very, b = broad, sh = shoulder.

DISCUSSION

The kinetics of isotope exchange between a well-stirred fluid phase and a bed of uniform spherical particles or an infinite plane sheet are well understood theoretically. Berthier(22) has given a mathematical analysis of the problem of determination of diffusion coefficients in solids by heterogeneous isotope exchange using a radioactive tracer. This followed upon the earlier work of Duenwald and Wagner(23) and Zimens.(24) Crank(25) portrays Berthier's results in the form of graphs of the fraction of solute taken up from a stirred solution of limited volume by a sphere of radius a or an infinite plane sheet of thickness 2L vs $(Dt/a^2)^{1/2}$ or $(Dt/L^2)^{1/2}$, respectively, for various values of the fraction of solute finally taken up by the sphere or sheet. For the case of the sphere, in the limiting case of an infinite volume of solution (zero final fractional exhaustion of solute from solution), it may readily be shown that for small t, the fractional uptake is linear in $(Dt/a^2)^{1/2}$, with an initial slope of 3.39. For finite volumes of solution (i.e., non-zero values of the final fractional exhaustion), the curves of fractional uptake are initially nearly linear in $(Dt/a^2)^{1/2}$, with higher initial slopes.

Provided a homogeneous sample of spherical particles were available, the determination of the isotopically averaged diffusion coefficient for the proton in α-AlOOH would consist in a comparison of the initial slope of a curve of fraction of deuterium exchanged vs $t^{1/2}$ with the appropriate slope from Figure 6.4 of Ref. 25. The diffusion coefficient would then be $D = (as_2/s_1)^2\ \text{cm}^2\,\text{sec}^{-1}$, where s_2 is the observed initial slope ($\text{sec}^{-1/2}$), s_1 is the slope of the theoretical curve (no units) and a is the particle radius (cm).

Due to the dependence of D upon the square of the particle radius and the necessity of proper averaging over the particle size distribution function, it is not feasible to attempt an evaluation of the diffusion coefficient for the present case. However, from the temperature dependence of the exchange rate (using boehmite of constant particle size distribution) it is possible to determine the activation energy for the diffusion coefficient, defined as $E_D = -R\dfrac{d(\ln D)}{d(1/T)}$. Since $d(\ln D) = 2d(\ln s_2)$, the activation energy for the diffusion coefficient is twice the activation energy for the initial isotope exchange rate s_2. Using the value of 5.8 ± 1.3 kcal/mole (from Figure 2) the activation energy for the proton (deuteron) diffusion coefficient in boehmite is thus found to be 11.6 ± 2.6 kcal/mole.

The conductivity and proton mobility in polycrystalline ice has been measured by Spernol.(26) Below -15°C an activation energy of 3.9 ± 0.2 kcal/mole was obtained for the mobility. Using the Einstein relation between the diffusion coefficient D and mobility v: $\left(\dfrac{kT}{e}\right)v$, the activation energy for proton diffusion is $E_D = E_V + RT$, which gives a value of 4.5 kcal/mole in the case of ice.

The results on boehmite must be regarded as very preliminary in view of the limited data available. A uniform sample of known crystallite size must be studied* under a variety of experimental conditions (e.g., various ratios of solid to liquid phases, different pH, a wide range of temperatures, etc.). It would appear worthwhile to obtain a reliable determination of the proton diffusion coefficient in boehmite, $D = D_0 \exp(-E_D/RT)$, in order to assess the role of proton migration in the aqueous corrosion of aluminum. The extension to other metal-water systems in which a coherent hydrous oxide corrosion product film is obtained would also be of interest.

The very slow exchange of O^{18} relative to that of deuterium with boehmite suggests independent migration of oxygen-bearing carriers (such as OH^-, H_2O or $O^=$) and protons (deuterons) through the lattice.

In an X-ray diffraction crystallographic study of boehmite powder, Reichertz and Yost(27) noted the analogy with the lepidocrocite structure(28) and suggested that the boehmite crystal consists of aluminum-centered, distorted octahedra (oxygen atoms at apices), joined by sharing of edges into two-dimensional infinite layers, with successive layers held by hydrogen bonds. As in the case of lepidocrocite, one-half the oxygen atoms (labelled O_I) could be assigned to Al-O-Al links while the other half (O_{II}) were associated with hydrogen bonds (Al-O-H-O-Al bridges). It was suggested that cleavage of boehmite crystals occurred along the planes (sheets) of hydrogen atoms in the hydrogen bonds, giving orthorhombic plates.

It is postulated there that (1) hydrogen diffusion occurs along the sheets of bonded hydrogens, and (2) the observed oxygen exchange is limited to the O_{II} atoms, accessible through the sheets of hydrogen bonds. Further experiments are required in order to confirm the preliminary results which indicated that only half the oxygen atoms in boehmite are exchangeable.

It appears that further work on the crystal structure of boehmite is also needed before a detailed understanding of the diffusion process is possible. The unusually short hydrogen-bonded oxygen-oxygen distance of 2.47 Å in boehmite reported by Reichertz and Yost appears to be subject to considerable doubt. Nakamoto et al.(29) have shown a convincing correlation of OHO vibration frequencies with the OHO bond distance, which would imply that such an unusually short bond would be associated with an OH frequency very much lower than that observed (Table I and Figure 6); the observed frequency is, however, in the "normal" range for hydrogen bonded OH frequencies corresponding to an O-O distance of about 2.76 Å, similar to that found in lepidocrocite (2.71 Å). It seems probable, however, that the sheet structure of boehmite is correct, so that the qualitative picture of migration along sheets of H-bonds is probably valid.

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*Note added in proof: Experiments by Y. K. Wei and the author are now in progress to evaluate the proton diffusion coefficient in boehmite of known particle size.

In the light of the deuterium exchange results it is of interest to consider the corrosion-exchange experiment. The slow rate of deuterium exchange with the growing boehmite film may be due in part to impurities (Fe and Si) present in the aluminum, which may enter into the α-AlOOH lattice in such a way as to reduce the proton mobility. Corrosion-exchange studied with pure (> 99.99%) aluminum are needed in order to establish a possible relationship between proton mobility in the barrier film and the rate of the corrosion reaction. It is suggested that the isotope exchange technique could be extended to investigate the general problem of ionic mobility in barrier films.

It should be noted that a somewhat analogous corrosion-exchange study by Winter(30) involving exchange of O^{18} labelled oxygen gas with a growing cuprous oxide film at elevated temperatures indicated very little exchange under conditions when film growth was measureable.*

Another area suggested for future investigation is the application of the kinetic isotope effect to the study of corrosion reactions. The deuterium isotope effect in the reaction of water vapor with zinc has been studied in the neighborhood of 400°C, where an isotope effect, $k_H/k_D = 1.6$, was found.(33) This was attributed to a rate-determining step involving the rupture of an oxygen-hydrogen bond in water. In the reaction of gaseous oxygen with copper, it is known(34,35) that O_2^{16} reacts preferentially compared to $O^{16}O^{18}$ (i.e., O^{16} concentrates in the Cu_2O film with a fractionation factor of 2-4%). The origin of the fractionation effect is thought to lie in a step involving rupture of an oxygen-oxygen bond.

In an attempt to utilize this technique in connection with the problem of the aluminum corrosion reaction in water, Mori and Draley(36) have recently measured the rate of corrosion of aluminum type 1100 sheets in D_2O (relative to a control series in H_2O) at 100°C. No significant isotopic effect in the steady-state rate (the "corrosion rate") was observed, although the magnitude of the total corrosion (largely determined by the initial rapid reaction preceding the nearly zero-order protective film stage) was significantly greater in H_2O. This result would suggest that the rate-determining process in the steady-state reaction at 100°C does not involve an O-H bond rupture or the diffusion of a proton (or deuteron) through an intact "protective" film of boehmite; in these cases a significant kinetic isotope rate factor

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*This is in agreement with the generally accepted Wagner parabolic mechanism in which the diffusing ions are thought to be cuprous ions migrating through the cation-deficit oxide lattice. Independent and direct evidence confirming this consisted of the measurement of the diffusion coefficient of Cu^+ ions in Cu_2O(31,32) using radioactive copper; the activation energy for the diffusion coefficient (38 kcal/mole) agreed well with that for the parabolic oxidation rate constant.

would be expected. Further isotopic rate studies would appear to be useful in elucidating the corrosion mechanism under other experimental conditions.

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