The Sodium Isotopic Exchange Rate between High-temperature Phases of Disodium Zirconium(IV) Bis(orthophosphate) and Aqueous Solutions

Yasushi INOUE* and Yoshimune YAMADA
Department of Nuclear Engineering, Faculty of Engineering, Tohoku University, Aramaki-aza-Aoba, Sendai 980

(Received July 25, 1983)

A monohydrate (Phase II) and three anhydrous phases prepared by the thermal treatment (at 250, 700, and 900 °C respectively for Phases III, IV, and V) of disodium zirconium(IV) bis(orthophosphate) trihydrate were studied from the sodium isotopic exchange rate between them and aqueous solutions. In Phases III and IV, which had been sufficiently adapted in water in advance, the rate was found to be controlled by the diffusion of sodium ions along the direction perpendicular to the layers consisting of zirconium atoms and the diffusion constants, and their activation energies (for Phases III and IV, 57 and 52 kJ/mol) were evaluated. When these phases were used as dried, the rate was governed by the irreversible dissociation of sodium in the solid phases. In Phase II, used as dried, and in Phase V, used as dried and wetted, the rate was controlled by neither particle diffusion, film diffusion, nor chemical reaction alone. This behavior was attributed to the complex behavior of phase transformation as the isotopic exchange proceeded.

The dehydration of the disodium zirconium(IV) bis(orthophosphate) trihydrate (hereafter this material will be referred to as Phase I) obtained from the zirconium(IV) bis(hydrogenphosphate) monohydrate prepared by the direct precipitation method[1] was found to give a monohydrate and three anhydrous phases, depending on the temperature of thermal treatment and on the surrounding humidity. The most suitable conditions for the preparation and for the storage of these five phases, including Phase I, were also established in addition to the examination of phase transformation brought about by immersing them in aqueous solutions.[2]

As Phase I is the most stable of them at room temperatures, it was at first used for the study of the sodium isotopic-exchange rate to provide fundamental data which would be useful for elucidating ion-exchange kinetics. It was concluded that the rate was controlled by the particle diffusion along the direction perpendicular to the layers of crystals; the diffusion constants and their activation energies were obtained as has previously been described.[3]

Since this type of material, known as "crystalline zirconium phosphate", can be used as an ion exchanger at high temperatures, the study of ion-exchange kinetics for its high-temperature phases is interesting. The rate for them acquires additional interest from the facts that their structures differ in different phases and that the capillary water introduced by placing them in contact with aqueous solutions plays an important role in the rate of the exchange.

This paper will deal with the radiochemical experiments performed to measure the isotopic-exchange rate of sodium ions between $Na_2Zr(PO_4)_2 \cdot nH_2O (n=0, 1)$ and concentrated sodium nitrate solutions and will discuss the results with reference to their phase stability in aqueous solutions.[2]

Experimental

Preparation of the Materials Spiked with ^{22}Na. Phase I labeled with ^{22}Na at about 40 μCi/g(1 Ci=3.7×10^{10} Bq), with uniform crystal sizes, was prepared by the procedure reported previously.[3] Its average size is given in Table 1. The radiochemical purity of ^{22}Na was confirmed by gamma-ray spectrometry. The monohydrate (Phase II) was obtained by drying Phase I over P_2O_5 for three weeks, while the anhydrous phases, phases III, IV, and V, were formed by heating Phase I at 250, 700, and 900 °C respectively for 4 d.[2] They were stored *in vacuo* over P_2O_5 and used for the rate measurement (as a dried system). In addition, parts of them were immersed in water for a definite period of time (Phases III and IV, 1 d; Phase V, one week) to adapt them to aqueous solutions and then also used for the experiments (wet system).

TABLE 1. PARTICLE SIZE OF THE SAMPLES

No.	Mean crystal size/μm		
	Length	Width	Thickness
1	286±44	238±32	16±3
2	190±24	159±15	16±2

The Measurement of the Isotopic-exchange Rate. All the experiments were performed in a nitrogen atmosphere. The rate was measured by using the same apparatus as before.[3] A 400-mg portion of the sample was placed in the cage and immersed in 200 cm^3 of a 5-mol dm^{-3} sodium nitrate solution, whose pH was adjusted to 11 by sodium hydroxide, while the cage was rotated at a rate of 1200 min^{-1}. The solution had been adjusted in advance to a constant temperature within ±0.1 °C. Aliquots of the solution (about 0.2 cm^3) were taken out at appropriate time intervals in order to measure the radioactivity with a well-type NaI(Tl) scintillation counter. The time of contact of the solution with the exchanger was taken as the time which elapsed between the immersion of the cage and the withdrawal of an aliquot of the solution.

The fractional attainment of equilibrium, $F=C_t/C_\infty$, was calculated from these results; here, C_t is the total radioactivity of the solution at time t and C_∞ at $t=\infty$. C_∞ was calculated by means of this equation; $C_\infty=CM/(M+m)$, where C is the initial total radioactivity of the exchanger and where m and M are the total amounts of Na^+ ions in the exchanger and in the solution respectively. After the experiments were finished, it was confirmed microscopically that the particles did not break down at all during this series of procedures.

The other materials, apparatus, and experimental proce-

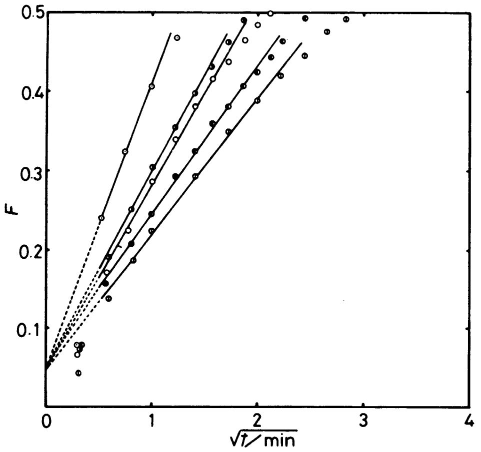

Fig. 1. Isotopic exchange rate for Phase III (wet system). pH 11, 5 mol dm^{-3} NaNO$_3$.
⦿: 19.6 °C, sample 2, ◑: 12.5 °C, sample 1, ○: 9.5 °C, sample 2, ◐: 5.0 °C, sample 2, ⦶: 1.3 °C, sample 1.

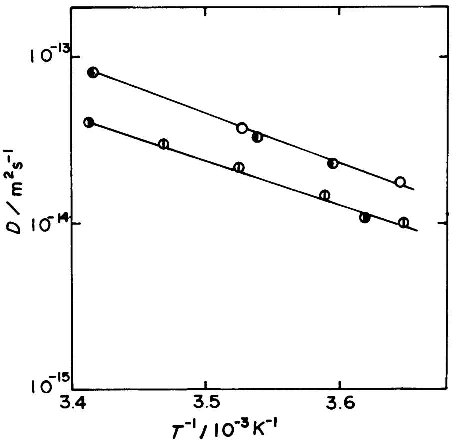

Fig. 2. Arrhenius plot of D for Phases III and IV (wet system).
pH 11, 5 mol dm^{-3} NaNO$_3$.
○: Phase III, sample 1, ◐: Phase III, sample 2, ◑: Phase IV, sample 1, ⦶: Phase IV, sample 2.

dures were the same as had been described previously,[3] except as otherwise noted.

Results and Discussion

The sodium isotopic-exchange rate was measured with two types of samples: (a) dried and (b) wet. The results for each type of experiment will be described separately for convenience.

Wet System. The fractional attainment of equilibrium, F, against the square root of the time needed for Phase III is shown in Fig. 1. For Phase IV, curves similar to Fig. 1 were also obtained, though the rate was slower for Phase IV than for III. This figure clearly indicates that a linear relation held between F and $\sqrt{t}$ in the F range smaller than about 0.4 except for the initial portion of these plots. The curves also reveal that the rate was independent of the particle size. In this manner, the dependence of the rate on various experimental factors for Phases III and IV is similar to that for Phase I; hence, we can analyze the data by applying the same assumptions made for Phase I, that is, the rapid attainment of exchange equilibrium on the surface of the crystals, followed by a slow diffusion into the bulk of them, a diffusion along the direction perpendicular to the layers consisting of zirconium atoms. The diffusion constant, D, can, therefore, be obtained from F by means of this equation;

$$F = \frac{2}{\pi^{1/2}}\sqrt{\beta t}.$$

where $\beta = D/l$, and l is the half-thickness of the crystals.[3] For calculating D, a revised value of l was used in place of that presented in Table 1. When Phase I is transformed to Phase III, the interlayer distance decreases from 0.983 to 0.839 nm.[2] This inevitably shortens the thickness of the crystals to 0.839/0.983×16=13.7 nm. When log D was plotted against $1/T$, a good linearity was obtained, as is shown in Fig. 2. From the Arrhenius equation, $D = D_0\exp(E_a/RT)$, the activation energy and the constant, D_0, were evaluated. The values of D_0 for Phases III and IV respectively were 1.1×10^{-3} and 9.5×10^{-5} m^2/s, while those of E_a were 57±3 and 52±5 kJ/mol. It is not strange that the diffusion constants and their activation energies for these phases are about the same, for Phase IV is transformed to Phase III immediately after being immersed in water.[2] The slightly higher activation energy for Phase III than for IV can be explained in terms of the lower diffusion barrier in the latter, since the latter has more crystal defects than the former.[2] The exchange rate is much faster for Phases III and IV than for Phase I, and the activation energy of particle diffusion in these anhydrous phases has values about half that in Phase I (101 kJ/mol).[3] These differences cannot be attributed to the difference in the size of the openings, which interconnect the layers and which have a diameter of 0.24 nm at the largest, large enough to allow sodium ions to diffuse across the layers. Phase I contains three molecules of water of crystallization per formula, while the anhydrous phase has only a small amount of capillary water. Phase I, therefore, requires sodium ions to travel as large hydrated ions instead of free sodium ions, the species participating in the diffusion in the anhydrous phases. The difference between the trihydrate and anhydrous phases, therefore, results from the difference in the size of the ions traveling through the layers.

The F *vs.* $\sqrt{t}$ plots for Phase V are shown in Fig. 3, which indicates that no linearity held and that the rate slowed down abruptly after 60 min. This relation cannot be explained by the diffusion mechanism alone, but it might be due to the slow transformation of the crystals as the exchange proceeds.

Dried System. Contrary to the rate for the wet system, Phases III and IV when dried did not show a linear relation between F *vs.* $\sqrt{t}$, but they did show one between $-\log(1-F)$ and t, as is shown in Figs. 4 and 5. This means that the exchange rate is not controlled by the particle diffusion, but by either film diffusion or a chemical reaction. The film diffusion, however, does not appear to control the rate under the conditions adopted in the present experiments, *i.e.*, a high sodium-

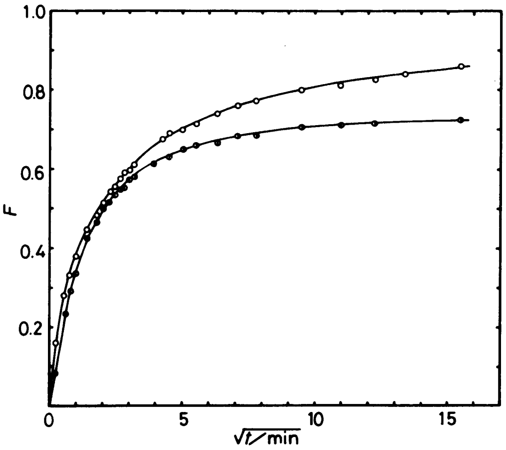

Fig. 3. Isotopic exchange rate for Phase V (wet system). pH 11, 5 mol dm^{-3} NaNO$_3$, sample 2.
○: 17.4 °C, ◑: 4.5 °C.

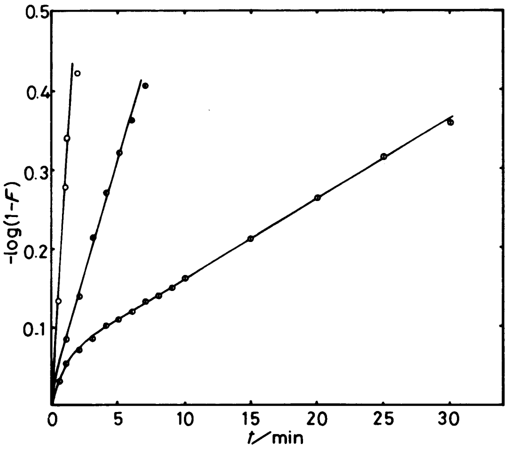

Fig. 4 Isotopic exchange rate for Phase III (dried system).
pH 11, 5 mol dm^{-3} NaNO$_3$, sample 2.
○: 44.7 °C, ◐: 24.9 °C, ◑: 5.9 °C.

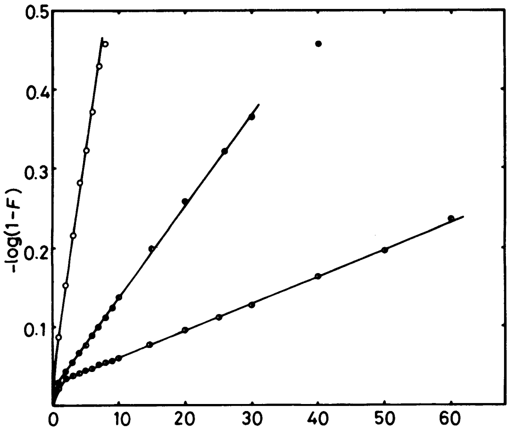

Fig. 5. Isotopic exchange rate for Phase IV (dried system).
pH 11, 5 mol dm^{-3} NaNO$_3$, sample 2.
○: 41.0 °C, ◐: 18.7 °C, ◑: 4.5 °C.

ion concentration and a high stirring speed in the range where it does not affect the exchange rate. Moreover, if the rate is controlled by the film diffusion, it must be faster for a dried than for a wet system. The experimental data, however, do not support this assumption. From these considerations, it can reasonably be assumed that the rates for the dried Phases III and IV are governed by a chemical reaction. The sodium in completely dried samples is considered to be strongly bonded with phosphate groups and not to be dissociated. As an ion-exchange reaction occurs between dissociated ions in the crystals and those present in the solution, sodium must be dissociated before the ion-exchange reaction commences.

If sodium is dissociated irreversibly with the rate constant, k, and if the sodium ions thus formed participate in the isotopic exchange reaction, that is,

$$\overline{\mathrm{RA}} \xrightarrow{k} \overline{\mathrm{R}} + \overline{\mathrm{A}^+}$$

$$\overline{\mathrm{A}^+} + \mathrm{B}^+ \overset{K}{\rightleftarrows} \mathrm{A}^+ + \overline{\mathrm{B}^+}$$

$$K = \frac{m_\mathrm{B}C_\mathrm{A}}{m_\mathrm{A}C_\mathrm{B}}.$$

From the material balance,

$$m_\mathrm{RA} + m_\mathrm{R} = E,$$

$$m_\mathrm{R} = m_\mathrm{A} + m_\mathrm{B},$$

where R$^-$ is the matrix of the exchanger; K, the equilibrium constant of the exchange reaction; m, the amount of designated species in the exchanger; E, the specific ion-exchange capacity, and C, the concentration of designated species in the solution, and where a bar refers to the solid phase.

From the experimental conditions, $C_\mathrm{A}/C_\mathrm{B}$ is always unity. Thus,

$$m_\mathrm{RA} = E - m_\mathrm{A} - m_\mathrm{B} = E - \frac{1+K}{K}m_\mathrm{B}.$$

The rate of increase of m_B can be written by;

$$\frac{\mathrm{d}m_\mathrm{B}}{\mathrm{d}t} = K\frac{\mathrm{d}m_\mathrm{A}}{\mathrm{d}t} Kkm_\mathrm{RA} = KkE - k(1+K)m_\mathrm{B}. \quad (1)$$

By integrating Eq. 1, we obtain:

$$m_\mathrm{B} = \frac{1}{k(1+K)}\,[KkE - \exp\{-k(1+K)t+g\}], \quad (2)$$

where g is the integration constant.

By applying the initial conditions, t=0, and m_B=0, Eq. 2 becomes;

$$Q = m_\mathrm{B} = \frac{KkE}{k(1+K)}[1-\exp\{-k(1+K)t\}], \quad (3)$$

$$Q_\infty = \frac{KkE}{k(1+K)}.$$

When we set $Q/Q_\infty = F$, we obtain:

$$\log(1-F) = -\frac{k}{2.303}(1+K)t.$$

In the isotopic exchange, K=1; therefore,

$$\log(1-F) = -\frac{2k}{2.303}t. \quad (4)$$

Equation 4 agrees with the results of the experiments.

Even when the dissociation reaction proceeds reversibly, Eq. 4 is valid. If we consider that the dissociation

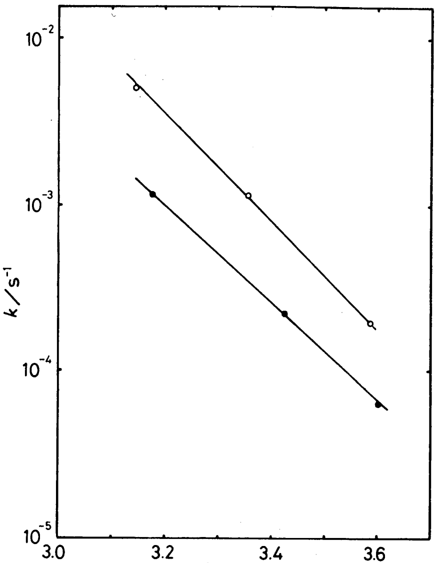

Fig. 6. Arrhenius plot of k for Phasses III and IV (dried system).
pH 11, 5 mol dm^{-3} $NaNO_3$, sample 2.
○: Phase III, ●: Phase IV.

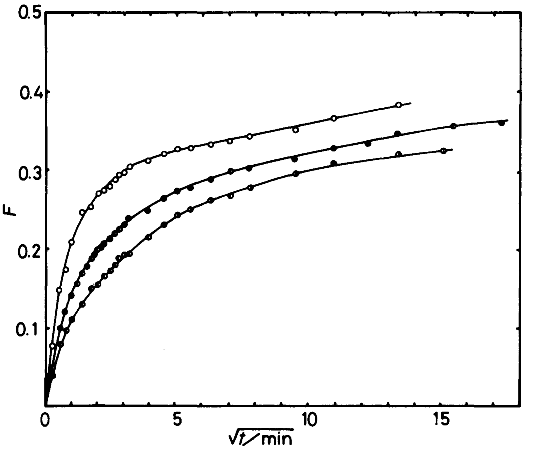

Fig. 7. Isotopic exchange rate for Phase II (dried system).
pH 11, 5 mol dm^{-3} $NaNO_3$, sample 2.
○: 44.3 °C, ◐: 18.7 °C, ⦶: 4.9 °C.

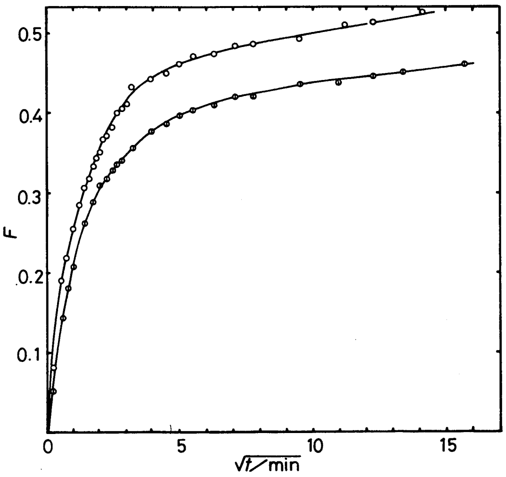

Fig. 8. Isotopic exchange rate for Phase V (dried system).
pH 11, 5 mol dm^{-3} $NaNO_3$, sample 2.
○: 18.4 °C, ⦶: 5.4 °C.

reaction is reversible, the same relation must hold for a wet system. However, as the isotopic-exchange reaction for a wet system is much faster than this and is controlled by the particle diffusion, the reversible dissociation cannot be rate controlling. Accordingly, when the completely dried Phases III and IV are in contact with the solution without having been wet in advance, the rate of exchange reaction is controlled by the irreversible dissociation of sodium in the exchanger, which is much slower than the particle diffusion.

The reaction rate constants, k, were obtained from the slopes of the straight lines in Figs. 4 and 5; they are plotted against $1/T$ in Fig. 6. The activation energies of the dissociation reaction for Phases III and IV were 63±2 and 56±2 kJ/mol respectively, while the frequency factors of the Arrhenius equation, k_0, are 1.2×10^8 and 2.6×10^6 s^{-1}. The faster reaction rate for Phase III than for IV can be ascribed to the lower temperature of the thermal treatment of the former.

The plots of F against $\sqrt{t}$ for Phases II and V are shown in Figs. 7 and 8. Contrary to Phases III and IV, neither these plots nor the plots of $-\log(1-F)$ *vs.* t are straight lines; hence, the rate is governed by neither film diffusion, particle diffusion, nor a chemical reaction alone.

In the case of Phase II, the rate slowed down markedly with the progress of the exchange. The rate will be controlled at first by the faster diffusion in Phase II, followed by the slower diffusion in Phase I, which is formed as the exchange reaction proceeds.[2] In other words, the curves may result from a complicated combination of the transformation rate of the crystals and the diffusion of ions in them.

Figure 8 indicates that the isotopic-exchange rate for Phase V behaved similarly to that for Phase II and was slower than that for a wet system. The reason for this rather complicated behavior is not clear, but it may be due to the complex behavior of the transformation of this phase.[2]

Further investigations must be undertaken before the kinetics of the sodium isotopic-exchange reaction for Phases II and V can be unambiguously determined.

References

1) Y. Inoue and Y. Yamada, *Bull. Chem. Soc. Jpn.*, **52**, 3528 (1979).

2) Y. Inoue and Y. Yamada, *Bull. Chem. Soc. Jpn.*, **55**, 792 (1982).

3) Y. Inoue and Y. Yamada, *Bull. Chem. Soc. Jpn.*, **56**, 705 (1983).