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SODIUM ISOTOPIC EXCHANGE RATE BETWEEN CRYSTALLINE ZIRCONIUM PHOSPHATE AND MOLTEN $NaNO_3$

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The isotopic exchange rate of sodium ion between crystalline zirconium phosphate and molten $NaNO_3$ has been measured at 312°C and 362°C by batch method. The equilibrium was reached within 20 minutes at either temperature, and the rate was very rapid as compared with that of sodium-potassium ion exchange.

The ion exchange rate of sodium and potassium ions between crystalline zirconium phosphate (ZrP) and molten alkali nitrate has been recently reported by Italian scientists.1)-3) To understand their data, it is necessary to know whether the rate controlling step is simple diffusion or some other processes. In order to clarify this point, the isotopic exchange rate of sodium ion between ZrP and molten $NaNO_3$ was measured by using ^{22}Na as a tracer.

ZrP in the sodium form spiked with ^{22}Na was obtained by percolating 0.2M-(NaCl + NaOH) solution containing ^{22}Na (pH=10) through a column of the exchanger which was prepared according to the modified method of Alberti and Torracca4); a solution 0.015M in $ZrOCl_2 \cdot 8H_2O$, 9M in H_3PO_4 and 0.1M in HF was kept warm at 60°C for 144 hours. It was dehydrated by heating at 350°C for 2 days before use. The size of the exchanger particles was -150+350 mesh.

Isotopic exchange procedures were as follows: 200g of $NaNO_3$ was melted in a Pyrex cell (50^{ϕ}mm x 250mm) at a desired temperature controlled within ±4°C in a nitrogen atmosphere, and then weighed amount of the exchanger (0.5g) was added to the melt. About 0.5g of the melt was pipetted out repeatedly at proper time intervals, and its specific activity of ^{22}Na was then measured.

The degree of attainment of equilibrium, F, was calculated by means of the following relationship.

$$F = \frac{\text{Amount of exchange at time t}}{\text{Amount of exchange at infinite time}}$$

The error of the experiments was within ±2%.

F as a function of time at 312°C and 362°C is shown in Fig.1 and Fig.2 respectively. They show that an equilibrium is attained within 20 minutes at either temperature.

In the experiment on sodium-potassium ion exchange between ZrP and molten $NaNO_3$-KNO_3 at 450°C, Alberti et al.$^{2)}$ found that the time necessary to reach equilibrium was dependent either on the initial ionic form of the exchanger or on the composition of the melt, and was at least 2 days. Allulli et al.$^{3)}$ also found that from a kinetic point of view the ion exchange process could be divided into two stages and in all cases 50% conversion occurred after a few hours in molten $NaNO_3$-KNO_3 at a temperature between 300°C and 450°C.

The comparison of the sodium isotopic exchange with the sodium-potassium ion exchange shows that the equilibrium is reached far more rapidly in the sodium isotopic exchange than in the sodium-potassium ion exchange. From this difference, we can conclude that the rate of sodium-potassium ion exchange is controlled by any process other than simple diffusion, for instance, phase transitions as described by Allulli et al.

In order to give further explanation, it is necessary to measure the rate at the initial stage of exchange, but our present method is inapplicable to the pursuit of the exchange rate at time intervals of seconds.

At present, authors are devising the experimental method which makes it possible to measure F at the initial stage of exchange and the results obtained by the new method will be reported in the near future.

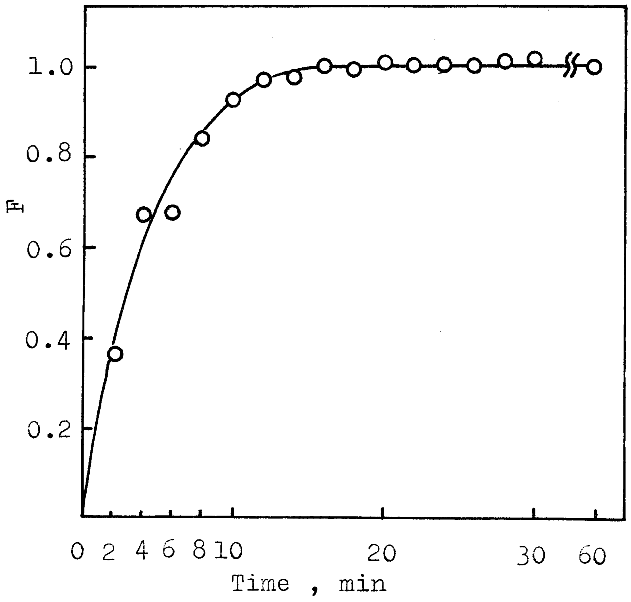

Fig.1 Sodium isotopic exchange rate between ZrP and molten $NaNO_3$ at 312°C.

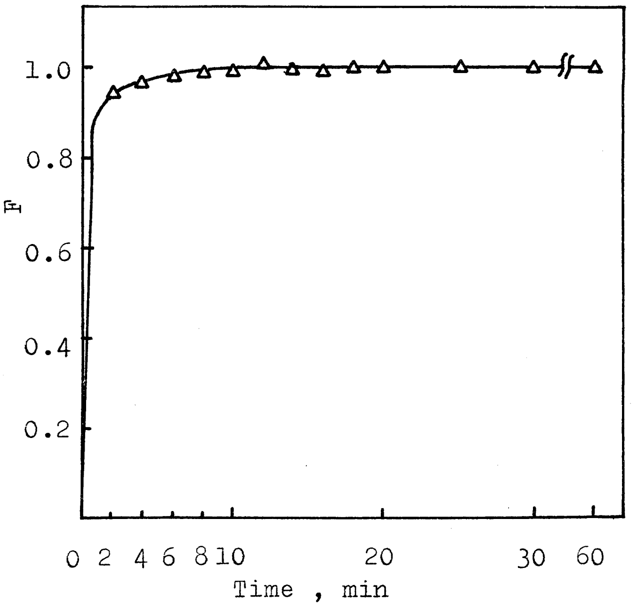

Fig.2 Sodium isotopic exchange rate between ZrP and molten $NaNO_3$ at 362°C.

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