SELF-DIFFUSION OF SOME CATIONS IN OPEN ZEOLITES

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ABSTRACT

Sodium, strontium and cesium self-diffusion coefficients in the natural zeolites erionite, phillipsite and clinoptilolite, and the synthetic zeolites Linde Type A and Type X are 1×10^{-9} cm²/sec to 5×10^{-7} cm²/sec in aqueous systems at 50° C. Activation energies were abnormally low in two instances. Helfferich's model for exchange kinetics in resins, including a nonconstant exchange diffusion coefficient, is applicable to zeolites.

INTRODUCTION

Cation diffusion in zeolites has been reported and discussed extensively in the literature. Barrer and Hinds (1953) reported exchange diffusion of sodium and thallium on analcime of 4.5×10^{-13} and 2.3×10^{-13} cm²/sec at 110° C. and 95° C., respectively. Barrer and Sammon (1955), gave some exchange rate curves for cesium, rubidium, thallium, barium, and silver cations on chabazite. Barrer *et al.* (1956) reported that silver cations replaced 85 per cent of the sodium on a synthetic faujasite (Linde $13\times$) within five minutes, and showed a self-diffusion curve for sodium in a synthetic faujasite. Several exchange diffusion coefficients for various feldspathoids are given in Barrer and Falconer (1956). Barrer and Rees (1960) reported some further diffusion studies with analcime. These authors concluded that the lack of correlation between sodium and potassium exchange rates and self-diffusion coefficients required further study. Barlow and Beattie (1962) measured the self-diffusion of sodium-22 in hydrated analcime and found an anomalously low diffusion coefficient and activation energy at low sodium molarities. Freeman and Stanmires (1961) and Stanmires (1962) studied extensively the electrical behavior of Type A and Type X in hydrated and partially hydrated pressed plates and derived several diffusion coefficients from the conductivity data.

METHODS OF INVESTIGATION

The purity and other properties of the synthetic Linde Type A and Type X, natural Nevada erionite and phillipsite, and Oregon clinoptilolite used in this study are the same as those used in several other studies (Ames, 1963, 1964).

The experimental apparatus was also described previously (Ames, 1962b). A 0.5g bed of zeolite was attached over a small opening in a shielded sodium iodide scintillation crystal. A solution containing only nonradioactive cation-chlorides was passed through the bed until solution-zeolite equilibrium was attained, as ascertained from previous trials with similar radioactive solutions (Ames, 1962a,b). A radioisotope was

then added to the same nonradioactive equilibrium solution and passed through the zeolite bed. The rate at which the radioisotope diffused into the zeolite was permanently recorded. The recording is similar to the curve shown in Fig. 1, which was corrected by the removal of the normal background count and counts emanating from the solution passing through the bed, leaving only the actual counts on the bed.

Solution concentrations were 0.2 normal. The solution immediately surrounding the zeolite particle did not tend to develop a concentration gradient (film diffusion) because the solution had reached equilibrium with the zeolite before the tracer was added.

The zeolite particles ranged in size from 0.25 to 0.50 and from 0.50 to 1.00 mm. A normal distribution within ranges was assumed in calculating an average grain size for each range.

After obtaining a curve, such as shown in Fig. 1, a self-diffusion coefficient can be simply derived if several conditions are met. The conditions include spherical, or nearly spherical, zeolite particles, that the change in composition of the solution and zeolite is negligible during the exchange, and that the concentration of traced cation at the zeolite particle surface be the same as the concentration of the traced cation in the
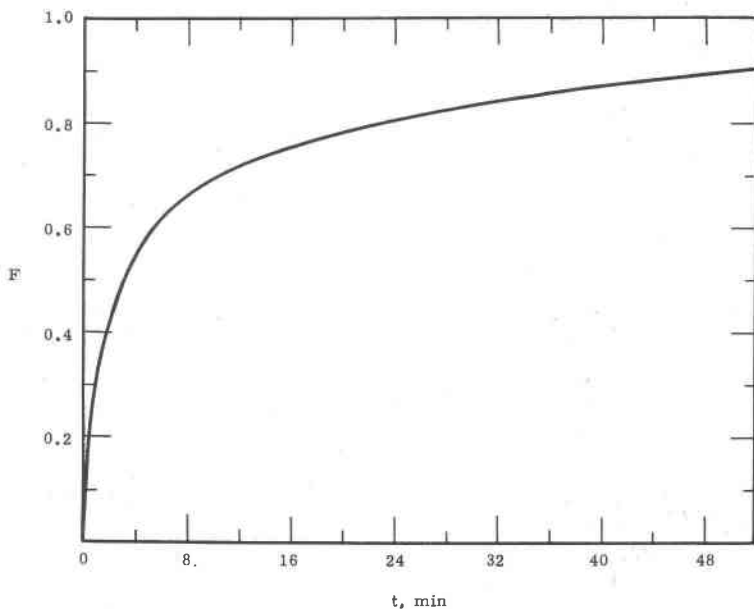

Fig. 1. Corrected curve for the isotopic diffusion of strontium-85 in Type X at 50° C. Average particle radius was 1.85×10^{-2} cm, time to 50 per cent exchange was 192 sec and bed weight was 0.5g.

solution. The equation that describes self-diffusion, or isotopic exchange, under the above conditions is given by Helfferich (1962) as:

$$U(t) = 1 - \frac{\overline{Q_A(t)}}{\overline{Q_{\bar{A}}}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp - \left(\frac{\overline{D} t \pi^2 n^2}{r_0^2}\right), \tag{a}$$

where

$U(t)$ = the fractional attainment of equilibrium at time t,

$\overline{Q_A(t)}$ = amount of cation A in the zeolite at time t,

$\overline{Q_{\bar{A}}}$ = initial amount of cation A in the zeolite,

r_0 = zeolite particle radius in cm,

$\overline{D}$ = a zeolite particle diffusion coefficient in cm²/sec., and

n = a dummy summation index.

At $t\frac{1}{2}$, or the time in seconds required to attain 50 per cent of equilibrium, equation (a) reduces to:

$$D = (0.030) \frac{r_0^2}{t\frac{1}{2}} \tag{b}$$

Thus the relative exchange rate is inversely proportional to the square of the zeolite particle radius.

The complete curve of fraction of attainment of equilibrium vs. time must be obtained in order to ascertain the 50 per cent point. Then the simplified equation (b) can be used and an apparent diffusion coefficient determined.

Determination of diffusion coefficients at two temperatures allows the computation of an activation energy.

Radioactive cations, sodium-22, cesium-134, strontium-85 and cerium-144 were obtained as high specific activity chlorides from the Isotopes Division of Oak Ridge National Laboratory. Reagent grade chemicals in distilled water solutions were used.

RESULTS

As shown above, the self-diffusion coefficient is a function of zeolite grain size. Consequently, two zeolite grain size ranges were used to determine an average self-diffusion coefficient. The self-diffusion values for the two size ranges are given in Table 1 as an indication of the good precision of the self-diffusion determinations. Average self-diffusion coefficients are given in Table 2 for single cations. The 70° C. values only represent determinations with a single zeolite size range.

Activation energies were computed, using the 50° C. and 70° C. self-diffusion values of the single cation systems, and the results listed in Table 3.

TABLE 1. SELF-DIFFUSION COEFFICIENTS IN CM²/SEC AT 50° C. IN TWO DIFFERENT
ZEOLITE GRAIN SIZE RANGES. TOTAL EQUILIBRIUM SOLUTION NORMALITY WAS 0.2

Cation System	Erionite	Oregon Clinoptilolite	Phillipsite	Type X	Type A
0.25 to 0.50 mm					
$Ce^{3+}-Ce^{144}$	——	——	——	2.46×10^{-9}	——
$Sr^{2+}-Sr^{86}$	2.77×10^{-8}	1.17×10^{-8}	9.55×10^{-9}	5.37×10^{-8}	8.19×10^{-9}
$Cs^{+}-Cs^{134}$	1.43×10^{-6}	1.91×10^{-7}	4.30×10^{-7}	1.15×10^{-7}	1.23×10^{-7}
$Na^{+}-Na^{22}$	2.46×10^{-7}	7.83×10^{-8}	3.44×10^{-7}	1.56×10^{-7}	6.87×10^{-8}
0.50 to 1.00 mm					
$Ce^{3+}-Ce^{144}$	——	——	——	2.33×10^{-9}	——
$Sr^{2+}-Sr^{85}$	2.77×10^{-8}	1.03×10^{-8}	9.44×10^{-9}	5.65×10^{-8}	8.63×10^{-9}
$Cs^{+}-Cs^{134}$	1.42×10^{-6}	2.02×10^{-7}	4.72×10^{-7}	1.87×10^{-7}	1.18×10^{-7}
$Na^{+}-Na^{22}$	2.72×10^{-7}	8.85×10^{-8}	4.14×10^{-7}	1.68×10^{-7}	7.68×10^{-8}

DISCUSSION

For several reasons, the self-diffusion values of this study fall in the
range of 1×10^{-9} to 1×10^{-7} cm²/sec while those of Barrer, *et al.* (1953,
1956, 1960, 1962) range from 1×10^{-11} to 1×10^{-15} cm²/sec. The chief
cause of the difference is that open zeolite structures are used in the

TABLE 2. AVERAGE SELF-DIFFUSION COEFFICIENTS IN CM²/SEC. TOTAL SOLUTION
NORMALITY WAS 0.2, WITH 0.1 NORMAL SOLUTIONS OF EACH CATION IN THE
CASE OF MIXED CATION SOLUTIONS. THE RADIOACTIVE CATION
IS THE MEASURED CATION IN EACH CASE

Cation System	Erionite	Oregon Clinoptilolite	Phillipsite	Type X	Type A
50° C.					
$Ce^{3+}-Ce^{144}$	——	——	——	2.40×10^{-9}	——
$Sr^{2+}-Sr^{85}$	2.77×10^{-8}	1.10×10^{-8}	9.49×10^{-9}	5.51×10^{-8}	8.41×10^{-9}
$Cs^{+}-Cs^{134}$	1.43×10^{-6}	1.97×10^{-7}	4.51×10^{-7}	1.52×10^{-7}	1.21×10^{-7}
$Na^{+}-Na^{22}$	2.59×10^{-7}	8.43×10^{-8}	3.79×10^{-7}	1.62×10^{-7}	7.28×10^{-8}
$Na^{+}-Ce^{+3}-Ce^{144}$	——	——	——	7.46×10^{-9}	——
$Na^{+}-Sr^{+2}-Sr^{85}$	2.03×10^{-7}	4.71×10^{-8}	7.44×10^{-8}	8.40×10^{-8}	3.44×10^{-8}
$Na^{+}-Cs^{+}-Cs^{134}$	9.02×10^{-7}	1.66×10^{-7}	5.09×10^{-7}	1.46×10^{-7}	1.28×10^{-7}
70° C.					
$Ce^{3+}-Ce^{144}$	——	——	——	3.82×10^{-9}	——
$Sr^{2+}-Sr^{85}$	3.18×10^{-8}	1.67×10^{-8}	1.81×10^{-8}	1.15×10^{-7}	3.58×10^{-8}
$Cs^{+}-Cs^{134}$	2.58×10^{-6}	2.87×10^{-7}	5.70×10^{-7}	4.91×10^{-7}	2.58×10^{-7}
$Na^{+}-Na^{22}$	5.73×10^{-7}	9.55×10^{-8}	5.30×10^{-7}	4.30×10^{-7}	1.43×10^{-7}

TABLE 3. ACTIVATION ENERGIES IN KILOCALORIES PER MOLE,
ROUNDED TO NEAREST 100 CALORIES

Cation System	Erionite	Oregon Clinopti- lolite	Phillip- site	Type X	Type A
$Ce^{3+} - Ce^{144}$	—	—	—	5.1	—
$Sr^{2+} - Sr^{85}$	1.5	4.6	7.1	8.1	15.9
$Cs^+ - Cs^{131}$	6.5	4.2	2.6	12.9	8.3
$Na^+ - Na^{22}$	8.7	1.5	3.7	10.7	7.4

present study. Analcime, for example, has only about half of the intra-crystalline void volume of Type A, erionite, phillipsite or clinoptilolite, and about one third that of Type X. As might be expected, diffusion rates are much faster in the relatively open zeolites, provided that channel constrictions between adsorption cavities are reasonably large.

Another factor in the relatively fast diffusion of this study was the physical nature of the zeolite sample, and the consequent method of diffusion measurement. Most of the above authors were measuring the self-diffusion of cations in single crystals of zeolite. The results, then, represented only intracrystalline self-diffusion. The zeolites of this study, on the other hand, also were of a certain particle size, but were composed of bundles of cemented zeolites crystals. The particles there-fore consisted of up to 60 per cent intercrystalline voids plus the intra-crystalline voids of the zeolite. The self-diffusion values given in this study represent intercrystalline diffusion, or diffusion within the liquid inside the zeolite particle but outside of the zeolite crystals, plus intra-crystalline diffusion within the zeolite crystals. However, intracrystalline diffusion is rate-controlling in any case and is very much faster in the open zeolites, as indicated previously by Barrer *et al.* (1956). It should be emphasized that most natural zeolites formed by alteration of vol-canic tuffs are cemented bundles of small zeolite crystals (Deffeyes, 1959; Hay, 1963a). The self-diffusion values given in this study would be more applicable to natural systems than other diffusion values representing intracrystalline diffusion only.

Several areas of interest are discernible in the self-diffusion data of Table 2. The effect of cation valence on self-diffusion rates is most prominent with self-diffusion coefficients decreasing from plus one to plus three cations. The same valence effect has been observed with the self-diffusion of cations in organic resins (Helfferich, 1962).

Self-diffusion rates in the open zeolites in this study are somewhat comparable to similar cation self-diffusion rates in highly-crosslinked, organic ion exchange resins. Soldano and Boyd (1953) for example, show

a sodium self-diffusion coefficient at 25° C. of about 2.4×10^{-7} cm²/sec in a sulfonated styrene-type resin of 16 per cent divinylbenezene. In several instances, the self-diffusion rates in zeolites are slower than those of the same cations in organic resins, but in no case are the self-diffusion rates in zeolites faster than in resins of the same particle size.

Helfferich and Plesset (1958) pointed out that any theory of particle diffusion kinetics must take into account the diffusion potential within the system. A nonlinear relationship was shown to exist between the exchanger diffusion coefficient within the zeolite ($\overline{D}_{AB}$) and the ionic composition of the zeolite, or

$$\overline{D}_{AB} = \frac{\overline{D}_A \overline{D}_B (Z_A{}^2 \overline{C}_A + Z_B{}^2 \overline{C}_B)}{\overline{D}_A Z_A{}^2 \overline{C}_A + \overline{D}_B Z_B{}^2 \overline{C}_B} \text{ (Helfferich, 1962, p. 269),} \tag{c}$$

where

$\overline{D}_A$ = the self-diffusion coefficient in the exchanger of ion species A,
$\overline{D}_B$ = the self-diffusion coefficient in the exchanger of ion species B,
Z_A = the charge on ion species A,
Z_B = the charge on ion species B,
$\overline{C}_A$ = the concentration of ion species A in the exchanger, and
$\overline{C}_B$ = the concentration of ion species B in the exchanger.

The assumptions contained in equation (c) are listed in Helfferich and Plesset (1958). Helfferich and Plesset also numerically evaluated equation (c) for univalent counter ions and six different mobility ratios. Figures 2 and 3 show the experimentally-determined and computed exchange rates for Type A and Type X, respectively, for the nonisotopic, sodium-to-cesium exchange. While the cation mobility ratios were not exactly those for which Helfferich and Plesset solved equation (c), the ratios were close enough, considering the experimental errors, to give a good indication of the applicability of equation (c) to zeolite exchanges. As can be seen from Figs. 2 and 3, equation (c) does adequately describe exchange curves in the two zeolite systems.

A further comparison was made between experimental and computed zeolite exchange rate curves from sodium to strontium on the zeolite. Plesset *et al.* (1958) gave numerical solutions of equation (c) for $Z_A/Z_B = \frac{1}{2}$ and $Z_A/Z_B = 2$, and six different ionic mobility ratios. Using the above solutions, a computed exchange rate curve was compared to the experimental curve as shown in Fig. 4. Although the experimental curve represents a somewhat slower exchange rate than the computed curve, the agreement is still good. Helfferich and Plesset emphasized that they expected actual ion exchange systems to deviate from their ideal limiting law.
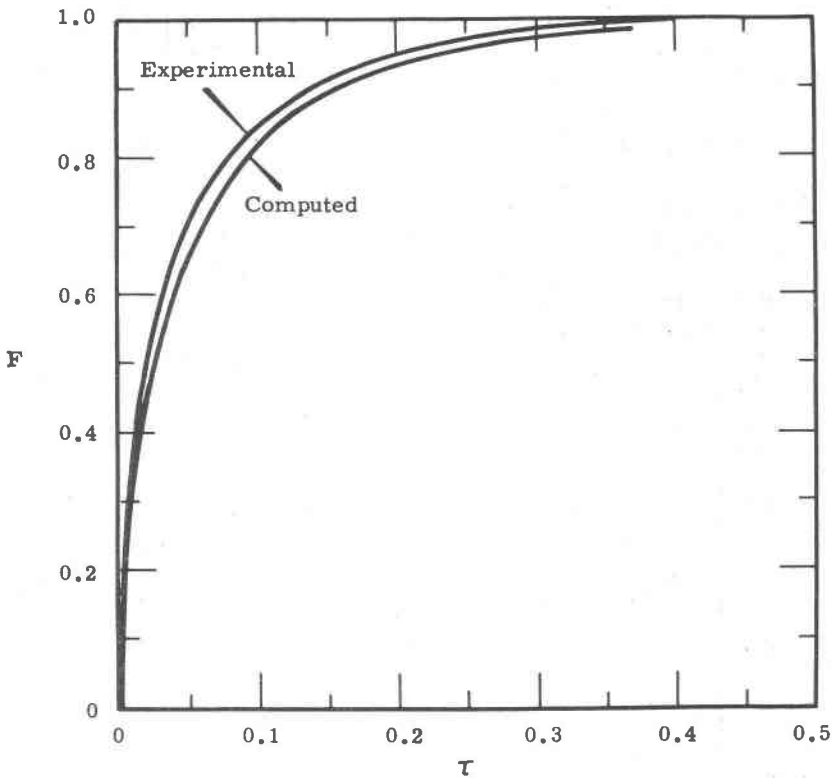
FIG. 2. Comparison of computed and experimental cesium exchange rate curves on Type A for the reaction $NaA + Cs^+ \rightleftharpoons CsA + Na^+$ at 50° C. The actual cation mobility ratio (D_{Na}/D_{Cs}) was 0.602, while the value 0.5 was used in calculating the computed curve. τ is a dimensionless time coordinate, $D_{Na}(t)/r_0^2$, where D_{Na} is the isotopic diffusion coefficient of sodium, t is the time in sec and r_0 is the zeolite particle radius in cm (1.85×10^{-2}). F is the fraction of cesium on the zeolite.

Zeolite particle diffusion data presented elsewhere (Ames, 1962a,b) represent nonisotopic exchanges. It should be noted that Reichenberg's treatment (Reichenberg, 1953) was used, which assumes a constant diffusion coefficient.

Helfferich (1962) contends that the exchange of a trace component can always be described by the rate laws of isotopic exchange, despite the fact that interdiffusion of two different counter ions may occur. Helfferich also noted, however, that this type of exchange did not result in a universal diffusion coefficient; *i.e.*, the trace ion self-diffusion coefficient was a function of the nature of the system. The effect on diffusion of adding a cation whose exchange rate is faster or slower than the ex-

change rate of the measured cation can be seen by examination of Table 2. Only one of the two cation diffusion rates were measured, but instances are given where the accompanying cations are both faster and slower in exchange rate than the traced cation. If a slower cation accompanies the traced cation, the resulting traced cation diffusion coefficient is slower than an isotopic diffusion coefficient without the presence of the accompanying cation. Conversely, if the accompanying cation is faster, the diffusion coefficient of the traced cation is likewise faster. Soldano and Boyd (1953) obtained similar results during a study of cation self-diffusion in Dowex 50-type resins.

There is a sodium self-diffusion value given in the literature that in-directly can be compared to a sodium self-diffusion value given in this study. Stanmires (1962) gives a value of about 3×10^{-8} cm²/sec at 25° C. for sodium self-diffusion in pressed Type X zeolite compacts, fully

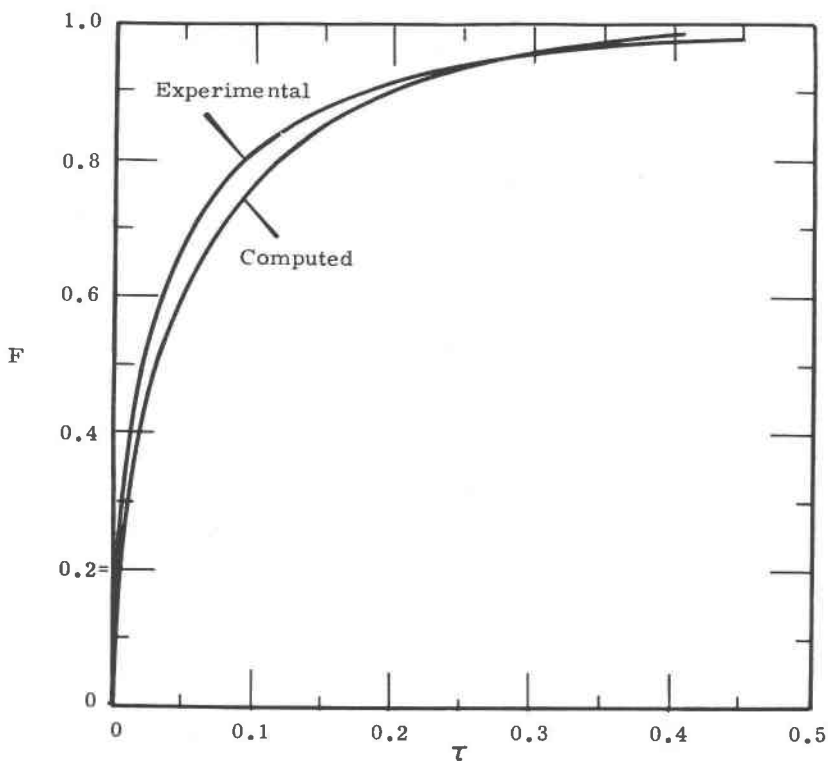

FIG. 3. Comparison of computed and experimental cesium exchange rate curves on Type X for the reaction $NaX + Cs^+ \rightleftharpoons CsX + Na^+$ at 50° C. The actual cation mobility ratio (D_{Na}/D_{Cs}) was 1.07, while the value 1.00 was used in calculating the computed curve. τ and F were defined in Figure 2.

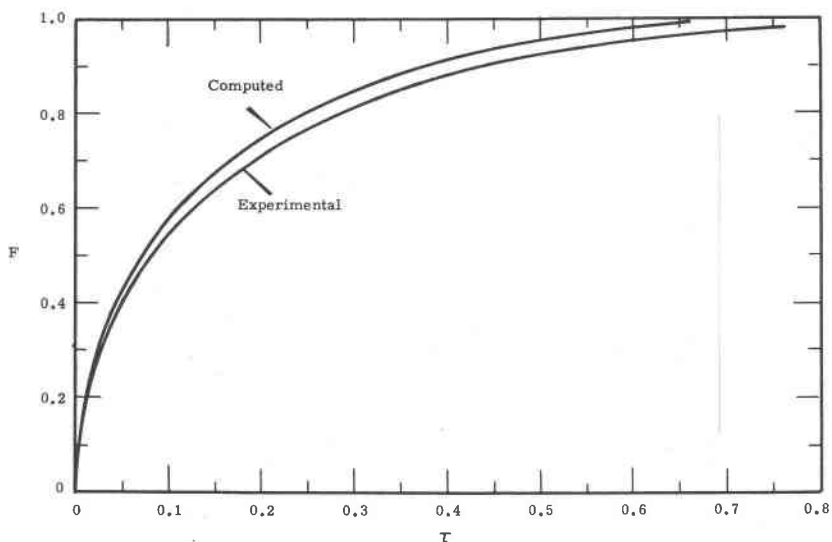Fig. 4. Comparison of computed and experimental strontium exchange rate curves on Type A for the reaction $Na_2A + Sr^{+2} \rightleftharpoons SrA + 2Na^+$ at 50° C. The actual cation mobility ratio (D_{Na}/D_{Sr}) was 8.66, while the value 10.0 was used in calculating the computed curve. τ and F were defined in Figure 2.

saturated with zeolitic intracrystalline water, similar in nature to the Type X pellets used in this study. If the sodium self-diffusion value of this study of 1.62×10^{-7} cm²/sec at 50° C. was adjusted to 25° C. and the intercrystalline water removed, the result would probably be very close to 3×10^{-8} cm²/sec. As Stanmires points out, his activation energies cannot be directly compared to those of this study.

Activation energies obtained for the natural zeolites, such as 1.5 kcal/mole for the self-diffusion of strontium in erionite, are unusually low. Activation energies in liquids do decrease with increase in temperature, though it is doubtful that such a decrease would account for the two lowest activation energies shown in Table 3. Normally, activation energies of from four to five kcal/mole result from increasing solution temperature alone. The activation energies obtained for the Type A and Type X are assumed to be valid. The high strontium self-diffusion activation energy of Type A also was obtained in an earlier study (Ames, 1962a).

Coombs *et al.* (1959) reviewed several aspects of the chemical alteration of volcanic tuffs to form zeolites. Essentially, the alteration of tuffs to zeolite-containing tuffs requires the contact of the tuff with relatively concentrated alkaline salt solutions under semiarid conditions. It is highly probable that a diffusion step is required for the altering salt solu-

tions to make intimate contact with all parts of the tuff. Assuming that a diffusion step is required, and that there was little or no volume change during the alteration process, the self-diffusion of sodium into the zeolite today can give an estimate of the shortest length of time required for alteration. Since an estimate of the time required to form a zeolitized tuff is available in the literature (Hay, 1963), we may compare the time required to diffuse sodium into the tuff with Hay's estimated age of Olduvai Gorge zeolitic tuff alteration of from 8000 to 20,000 years. In computing the sodium diffusion rate in the tuff, an average self-diffusion coefficient from three different zeolitized tuffs can be used in the relationship:

$\overline{X}^2 = 2Dt$, where

D = an apparent diffusion coefficient in cm²/sec,

t = time since the diffusion process began in sec, and

$\overline{X}$ = the average distance diffused in time t in cm.

For a sodium self-diffusion coefficient of 7.0×10^{-8} cm²/sec at 25° C., an average distance of 2.1 cm/yr would be traversed by the sodium ions. The actual traversed distance value is, of course, unknown but would be very much smaller than 2.1 cm/yr because rainfall at Olduvai Gorge is intermittent. Considering, then, that the effective sodium diffusion coefficient is about one-tenth, or less, of 2.1 cm/yr, or 0.21 cm/yr, it would require about 3630 years for sodium to diffuse to the maximum alteration depth of 25 feet of tuff mentioned by Hay. Of course, the rate of alteration of glass to zeolite after contact with the salt is unknown. The 3630-year value for diffusion time is not to be taken seriously since there are many unknowns and assumptions contained in it, but it is of interest that the alteration time estimates of both Hay and of this study are of the same order of magnitude. It is conceivable that diffusion alone could supply the alkaline salt environment necessary for tuff alteration.

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