Some Investigations in the Crystal Chemistry of Silicates

I. Diffusion of Pb and Ra in Feldspars

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The diffusibilities of ions in ionic crystals and atoms in metals and alloys have been studied during several decades by a great number of scientists, and valuable results on this research have been published. Barrer¹ gives a thorough list of references to the scientists who have worked in this extensive field of science.

The diffusibilities in crystal silicates, however, have chiefly been investigated in a qualitative way. The quantitative investigations have been concentrated on diffusion in zeolites. In *International critical tables* only one single quotation on the diffusion coefficient of ions in crystalline silicates is to be found. This concerns the diffusibility of Na^+ in natrolite at 20 degrees centigrade. The value given is $13 \cdot 10^{-6} \text{ cm}^2$ per day $= 11 \cdot 10^{-11} \text{ cm}^2$ per sec. There is no statement as to the energy of activation.

For a long time scientists have been aware of the fact that diffusion occurs more rapidly in zeolites like natrolite than in the usual crystalline silicates. This depends on the loose crystal structure of the zeolites and the high water content.

Bowen³ has measured the diffusion of diopside glass in different plagioclase glasses. He found that at about 1500 °C the diffusion coefficients vary from 0.015 to 0.3 cm^2 per day. His experiments must be considered as very elegant when the laboratory technique of that time is taken into account. As late as 1941 Eitel⁴ quoted his results as the only quantitative values of the diffusion coefficient in silicate glasses.

In a recent paper⁵ I have dealt with the diffusion of lead in some radioactive minerals. I found the following values:

$D_{\text{Pb}} = 4 \cdot 10^{-19} \text{ cm}^2$ per sec in amorphous niobates-tantalates of the metamict samarskite-yttrotantalites type.

$D_{\text{Pb}} = 1.10^{-18}$ cm² per sec in amorphous ortho-silicates of the metamict uranorthorites type.

$D_{\text{Pb}} = 2-4.10^{-22}$ cm² per sec in crystal uranium 4 oxide of the uraninite type from Ausel and Morogoro.

These values refer to the average diffusion of Pb₂₀₆ since the formation of the minerals up to the present time.

Several serious reasons indicate that the temperature of the minerals never was much above 100° C in this very extensive space of time.

Bowen⁶ discussed the possible rates of diffusion in silicate crystals. Basing his calculations on his previous investigations regarding the diffusibility in plagioclase glasses, he found it reasonable that the diffusion coefficient in crystal silicates would be lower than 10^{-9} — 10^{-10} cm² per sec at temperatures of 1400—1500 °C. Such maximal values seem reasonable even though the diffusion coefficient of course must vary greatly for different ions in the same crystal. Bowen³ states that his experiments on the diffusion in silicate glasses did not support the assumption of selective diffusion. His methods, however, could hardly be considered as very useful in the study of selective diffusion if the difference in diffusibility should not happen to be very high. From other investigations, however, it is known that the diffusion coefficient of different ions in the same crystalline medium may vary by several orders of magnitude at the same temperature.

By means of radioactive tracers it is possible to study diffusion processes by very much higher accuracy than it has been possible by the earlier methods. Hevesey and Seith⁷ may be mentioned among those who carried out fundamental research work in this branch. It does not seem, however, as if the radioactive tracer technique has been much employed in the case of crystalline silicates, especially not in the quantitative determination of the diffusion constants.

The usual method in the study of diffusion processes in solid state by means of radioactive tracers is to use alpha active tracers and to measure the alpha activity or the recoil particles from the tracer. When the tracer is placed on the surface of crystals, the alpha activity or the recoil activity decreases as the radioactive component diffuses into the crystal. Such a method involves several advantages in the mathematical treatment, as the range of alpha-particles in all solids is very small, and the range of recoil particles still smaller.

When beta and gamma-active radioactive tracers are used, we can not employ the same calculation methods. This is caused by the fact that the range of gamma rays and of beta rays of usual energy in crystals are much above the thickness of the crystal layers through which the radioactive ions will diffuse in a sufficiently short time. According to the method mentioned

below, the diffusion coefficient in solids may be determined by means of beta and gamma active tracers. The experiments are based on the following assumptions:

a) The diffusion coefficient of the radioactive tracers is much higher in glasses than in crystal silicates at the same temperature. Several experiments have shown that this assumption is correct;

b) The depth of the silicate crystals through which the radioactive ions are diffusing, is small compared to the range of the beta and gamma rays in the mineral. It is easy to conduct the experiments in such a way that this assumption proves to be correct. The range of the beta rays of average energy is several millimeters in the usual silicates, and after three months the average penetration depth of the diffusing ions is only a few hundred microns, provided the diffusion coefficient is as high as 10^{-12} cm² per sec.

c) The thermodynamic potential of equal concentrations of the radioactive component is the same independent of whether they are dissolved in the glass or in the crystalline substance. We do not know if this assumption is correct, but we will later return to this question.

Anyhow, I assumed in the beginning that the difference in free energy would be without importance in the experiments referred to. I found it reasonable to assume this chiefly because of the modern theories of structure of the glass. Comp. Eitel⁴.

According to these theories the structure of the glass does not differ very much from the structure of the crystalline silicates. In my experiments on the diffusion of Pb⁺⁺ and Ra⁺⁺ in potash feldspars (microcline) and in sodium-feldspars (albite) I thought it reasonable that the ions alien to the lattices would find themselves in nearly the same condition independent of phase. Closer investigations, however, showed that this 3rd assumption was not quite correct, and I had to introduce a factor of correction.

To investigate this, small drops of glass were melted on the surface of the feldspar crystals in the same way as was done in the diffusion experiments described in this paper. The glass drops contained small amounts of the radio-active tracers evenly distributed. The feldspar crystals with the glass drops were heated for sufficiently long time for the radioactive tracers to penetrate approx. 2/10—3/10 millimeters into the crystals. The glass drops were then carefully removed and the radioactivity of the crystals measured. Later on 1/100 of a millimeter of the crystal surface was removed by grinding, and the radioactivity was measured a second time. The thickness of the removed layer was controlled by micrometer. The difference in activity was compared with the radioactivity of the glass slide of the same thickness and the same cross-section. When such a thin layer as 1/100 mm was ground off, we may assume that the concentration of the radioactive tracer in this layer is equal to the boundary concentration. The ratio between the boundary concentration and the concentration in the glass slide could then be intro-

duced as a factor of correction in the equation 11, page 574 in the following mathematical treatment of the problem.

I will here take the opportunity to express my sincere thanks to Jan V. Garwick, cand.real. for his valuable help in the mathematical treatment of the problems.

We are basing our calculations on the three assumptions mentioned above, employing the following experimental technique: On the surface of the solid where the diffusion coefficient is to be measured, another material with a relatively high content of the radioactive component used as a tracer is placed assuring good contact. The solid, with the glass containing the tracer is heated to the experimental temperature for a sufficiently long time. After this the glass with the tracer is removed and the radioactivity of the crystalline body is measured.

If the radioactive components have not penetrated, very far, we may neglect the absorption in the material, and we have:

$$A = \frac{N}{\lambda} \quad (1)$$

Here N is the number of radioactive atoms which have penetrated into the solid. λ is the disintegration constant and A is the number of disintegrations per time unit. The radioactive atoms introduced in the solid are distributed in such a way that the equation:

$$\frac{\delta N}{\delta T} = D \nabla^2 N = D \frac{\delta^2 N}{\delta x^2} \quad (2)$$

is fulfilled. D is the diffusion coefficient. As a boundary condition we may find in several cases nearly

$$N = N_0 \text{ for } x = 0 \quad (3)$$

Here N_0 is the concentration in the glass. It is supposed that N_0 varies little with the time. This means that a very low fraction of the radioactive atoms has diffused out of the glass, and the diffusion coefficient in the glass is so high that the concentration variation is equalized by diffusion. When (2) and (3) are laplacetransformed and

$$L \{N(x, t)\} = n(x, s) \quad (4)$$

we have

$$D \frac{d^2 n}{dx^2} = sn \quad (5)$$

as

$$n = \frac{N_0}{s} \text{ for } x = 0 \quad (6)$$

$$N(x, 0) = 0$$

The solution of (5) passing towards 0 together with $\frac{1}{x}$ is

$$n = A \cdot e^{-\sqrt{\frac{s}{D}} x}$$

Here A is determined by (6) and we have:

$$n = \frac{N_0}{s} e^{-\sqrt{\frac{s}{D}} x} \quad (7)$$

We further have:

$$N(t) = q \int_0^\infty n(x, t) dx \quad (8)$$

Here q is the cross section of the surface through which the atoms are passing. This cross section is assumed to be great compared to the average penetration depth. (8) is laplacetransformed and we have

$$L\{N(t)\} = U(s) \quad (9)$$

Thus we have

$$U(s) = q \int_0^\infty n(x, s) dx = q \frac{N_0}{s^{\frac{3}{2}}} \sqrt{D}$$

where

$$N(t) = L^{-1}\{U(s)\} = 2 q N_0 \sqrt{\frac{Dt}{\pi}}$$

By direct measurement we have found A in (1). Hence we know

$$\frac{2_q N_0}{\lambda} \cdot \sqrt{\frac{Dt}{\pi}}$$

In order to determine N_0 we prepare a thin slide of the glass with a cross-section equal to q . If the thickness is d , this will contain qdN_0 radioactive atoms. We hence have $B = \frac{qdN_0}{\lambda}$ disintegrations per sec. The measurement of A and B will have the same errors for geometrical reasons, and in the ratio A/B ; these errors will then be eliminated. We therefore have

$$\frac{A}{B} = p = \frac{2}{d} \sqrt{\frac{Dt}{\pi}} \quad (10)$$

or

$$D = \frac{\pi}{4} p^2 \cdot \frac{d^2}{t} \quad (11)$$

It is supposed that the boundary concentration is equal to the concentration in the glass. If this is not the case, the factor of correction depending on the distribution coefficient must be introduced. This is most easily done by dividing the diffusion coefficient found, by the square of the distribution coefficient.

LABORATORY PROCEDURE

The first task was to prepare the glass containing radioactive tracers. The following two glass samples were prepared:

1. About 10 g of ordinary window glass was crushed and passed through a sieve (no. 60 U. S. Standard). The glass powder was carefully mixed with about two grams of lead oxide, containing about 4/1000 mC RaD. The mixture was melted in an iron crucible. After cooling, the glass charge was crushed again and remelted. This procedure was repeated 3 times in order to obtain a homogenous composition.

2. A second sample containing radium was prepared in much the same way. About 10 g of glasspowder was mixed with 0.5 g of carbonate of soda and 0.5 g of borax and 0.020 mg of RaBr_2 . This was dissolved in one milliliter of water. The different components were carefully mixed and after drying the mixture was melted in an iron crucible. In the same way as the first charge, the glass charge was remelted three additional times.

From the two glass charges small samples, weighing about 0.1 gram were taken out. Each sample was melted on a thin platinum sheet at about 1500° C until the sample was quite liquid. By means of a platinum rod the melted sample was spread evenly out on the sheet-metal in a thin layer. After cooling, the thin glass slide could be removed, and the thickness could be controlled by a micrometer.

Sample I an average thickness of 0.036 cm
 » II » » » » 0.024 »

This thickness is much below the average range of β and γ rays in the glasses, and no measurable weakening in the radiation because of absorption should occur. The two small glass slides were placed on non-radioactive vermiculite plates after weighing. They

were kept as radioactive standards. The radioactivity was measured 7 days after the preparation, and this radioactivity was noted. All the other samples dealt with in this paper were likewise measured 7 days after the last heat treatment. When any radioactivity is quoted, this hence refers to the activity after 7 days. In this way the major part of the errors depending on selective diffusion of different radioactive isotopes is eliminated. Likewise the possible error depending on the loss of Rn during the heat treatment is eliminated. All samples to be measured were placed exactly 0.5 cm below the center of the micawindow of the G. M. counter equipped with an end window. The activity was registered by means of an amplification circuit with scaling from 1 to 64. The mica window had a diameter of 1 inch and a weight of 0.03 g cm^{-2} . The glass slide containing RaD had a weight of 116.4 mg and a specific gravity 2.73. After 7 days the activity was $560.3 \text{ counts min}^{-1}$. The glass slide containing radium had a weight of 96.2 mg and a specific gravity of 2.65. After 7 days the activity was $2272 \text{ counts min}^{-1}$.

The crystals used in the following diffusion experiments were carefully picked from our mineral collection. The pieces could not be seen to contain any inclusions except perthites. As a sample of microcline, one piece of about 500 gr. from Elnerskilen in Evje was chosen; and as a sample of albite, a piece of about 300 g from Bjortjenn in Aust-Agder was used. The pieces were parted into smaller bits varying from about 1 cm^3 to about 15 cm^3 . From each mineral some pieces were ground and polished on different faces. The following faces were chosen: (001); (010) and $\perp$ [100]. The pieces were placed in a little furnace with the polished face upwards, and heated to a temperature of about 950°C . Small pieces of the radioactive glasses were placed on the faces. As soon as the glass had reached a sufficiently high temperature to weaken, the mineral pieces were removed from the furnace and cooled to room temperature. Usually less than one minute of heating was sufficient to weaken the glass. This time is too short to cause any measurable diffusion of the radioactive substances into the crystals.

The crystals thus provided with a glass drop on the polished face were placed in a furnace to be tempered at constant temperatures until sufficient quantities of the radioactive tracer had diffused into the crystals. The appropriate time had to be calculated from preliminary experiments.

After tempering, the mineral pieces were removed from the furnace and cooled to room temperature. The glass drops could then be removed from the mineral surface by means of a fine steel chisel. By means of a magnification glass the mineral faces could be examined. All traces of the glass drops had to be removed. Very often it happened that parts of the minerals had loosened when the glass drops were removed. In these cases the experiment was not continued, and in the tables only those results are given where visual examination showed no failures in the experiment. In the case of sodium feldspar it was especially difficult to remove the glass drop from the basis face without destroying the sample.

Seven days after the removal of the glass drops the radioactivity of the crystal face was measured. In the case of the potash feldspar the radioactivity of the feldspar was subtracted from the total activity. In the case of the albite the activity of the feldspar was so low that no subtraction was done. The diffusion coefficient was calculated according to formula 11, page 574. The activities of the standard glass slides mentioned were used as a comparative standard, and the standard glass slides were recalculated into slides of the same cross-section as the contact cross-section between glass and crystals.

THE DISTRIBUTION COEFFICIENT OF RADIUM AND LEAD BETWEEN GLASS
AND CRYSTALLINE FELDSPAR

The distribution coefficient resulting from diffusion was measured in the manner mentioned on page 572. The following results were obtained:

The potash feldspar distribution coefficient for Ra = 1.045
 » » » » » » RaD = 1.87
 » sodium » » » » » Ra = 1.3
 » » » » » » RaD = 1.15

After some preliminary experiments the following experiment was performed.

Table 1. Diffusion of lead in microclineperthite $\perp \{001\}$.

Expt. no.	Time	T	Tracer	Count min^{-1}	Cross- section of contact area in cm^2	Count cm^{-2} min^{-1}	D
11	90d	603°	RaD	36.0	2.4	15.0	$3.79 \cdot 10^{-14} \text{ cm}^2/\text{sec}$
12	90»	603°	RaD	13.6	0.8	17.0	$4.85 \cdot 10^{-14} \text{ cm}^2/\text{sec}$
15	6»	823°	RaD	8.3	0.25	33.3	$2.81 \cdot 10^{-12} \text{ cm}^2/\text{sec}$
16	6»	823°	RaD	13.2	0.25	52.8	$8.15 \cdot 10^{-12} \text{ cm}^2/\text{sec}$
17	44h	1023°	RaD	37.9	0.4	94.8	$7.28 \cdot 10^{-11} \text{ cm}^2/\text{sec}$
18	44»	1023°	RaD	41.5	0.4	103.5	$9.20 \cdot 10^{-11} \text{ cm}^2/\text{sec}$
19	44»	1023°	RaD	35.8	0.37	94.5	$7.22 \cdot 10^{-11} \text{ cm}^2/\text{sec}$
20	20»	1038°	RaD	31.5	0.8	39.4	$2.77 \cdot 10^{-11} \text{ cm}^2/\text{sec}$
21	20»	1038°	RaD	51.6	0.7	73.9	$0.74 \cdot 10^{-11} \text{ cm}^2/\text{sec}$

Standard sample 116.4 mg RaD-glass, specific gravity 2.73. Activity 560.3 count.
 min^{-1} , distribution coefficient 1.87.

Because of the relatively low value of the diffusion coefficient, the difference between parallel experiments may be considerable. Nevertheless, these differences are not so serious that the observations could not be used in calculating the activation energy and the diffusion constant D_0 . Fig. 1 shows a diagram where $\frac{1}{T} \cdot 10^4$ is marked along the x -axis and $\log_{10} D$ along the y -axis. The observations can be seen in relation to the theoretical values

Fig. 1. Diffusion of Pb^{++} in micropertchite $\perp \{001\}$.

$$D = 2.5 \cdot 10^{-6} e^{-\frac{21300}{RT}}$$

when $D_0 = 2.5 \cdot 10^{-6} \text{ cm}^2 \text{ sec}$ and $\omega = 21\,300 \text{ cal. per gramion}$. These values are introduced in the classical formula $D = D_0 \cdot e^{-\frac{\omega}{RT}}$.

In the later experiments the diffusion coefficient is higher, and the parallel experiments show a better agreement. Therefore I find it sufficient to perform 4 good experiments, at two different temperatures.

Table 2. Diffusion of lead in albite $\perp \{001\}$.

Expt. no.	Time	T	Tracer	Count min^{-1}	Cross-section of contact area in cm^2	Count $\text{cm}^{-2} \text{ min}^{-1}$	D
31	160h	873°	RaD	5.4	0.23	23.3	$4.68 \cdot 10^{-11} \text{ cm}^2/\text{sec}$
32	160h	873°	RaD	4.2	0.21	19.9	$3.52 \cdot 10^{-11} \text{ cm}^2/\text{sec}$
35	20h	1038°	RaD	30.3*	0.25	121	$3.22 \cdot 10^{-9} \text{ cm}^2/\text{sec}$
36	20h	1038°	RaD	53.3	0.40	133	$3.88 \cdot 10^{-9} \text{ cm}^2/\text{sec}$

Standard sample 116.4 mg RaD-glass, specific gravity 2.73. Activity 560.3 count/min. Distribution coefficient 1.15.

Fig. 2 shows a diagram where $\frac{1}{T} \cdot 10^{-4}$ is marked along the x -axis and $\log_{10} D$ along the y -axis. The observations show good agreement with the theoretical curve by introducing $D_0 = 2.5 \text{ cm}^2 \text{ per sec}$ and $\omega = 43\,200 \text{ cal per gramion}$.

Fig. 2. Diffusion of Pb^{++} in albite $\perp (001)$.

$$D = 2.5 \cdot e^{-\frac{43200}{RT}}$$

SURFACE DIFFUSION

In order to study the possible influence of surface diffusion in poly-crystalline aggregates, some experiments were tried. In these experiments a very finegrained leptite rich in feldspar was used. It proved however impossible to remove the glass drop quantitatively from this leptite without loosening parts of the leptite, and no reliable result could be obtained. For the time I therefore had to drop these experiments.

DIFFUSION ANISOTROPY

To investigate how the diffusion processes occur in different crystallographic directions in the two feldspar minerals, I measured the diffusibility of Ra^{++} . This tracer seems to be better suited for the experiment than was RaD . Lead feldspar seems to be isomorphically soluble in potash feldspar, but not in albite. Radium however, seems to be less soluble in potash feldspar, and the two feldspar minerals should therefore exhibit a more equal medium for diffusion. Because of the great radioactivity of the radium glass it was easier to get more accurate measurements in the case of radium than it was in the case of RaD .

Fig. 3. Diffusion of Ra^{++} in micropertite.

$$\begin{aligned}
 I \perp \{001\}. \quad D &= 5.1 \cdot 10^{-4} e^{-\frac{24300}{RT}} \\
 II \perp \{010\}. \quad D &= 2.4 \cdot 10^{-4} e^{-\frac{24000}{RT}} \\
 III \neq [100]. \quad D &= 2 \cdot 10^{-2} e^{-\frac{29200}{RT}}
 \end{aligned}$$

Table 3. Diffusion of Ra^{++} in micropertite.

Expt. no.	Time	T	Cryst. dir.	Tracer	Count min ⁻¹	Cross-section contact area in cm ²	Count cm ⁻² min ⁻¹	D
41	6d	823°	$\perp \{001\}$	Ra	205.3	0.42	854	$2.53 \cdot 10^{-10}$
42	6»	823°	$\perp \{001\}$	Ra	87.3	0.12	725	$1.82 \cdot 10^{-10}$
43	6»	823°	$\perp \{010\}$	Ra	87.5	0.14	620	$1.33 \cdot 10^{-10}$
44	6»	823°	$\perp \{010\}$	Ra	235.6	0.39	820	$2.32 \cdot 10^{-10}$
45	6»	823°	$\neq [100]$	Ra	150.20	0.11	1360	$6.35 \cdot 10^{-10}$
46	6»	823°	$\neq [100]$	Ra	281.30	0.20	1420	$6.94 \cdot 10^{-10}$
47	20h	1063°	$\perp \{001\}$	Ra	177.00	0.10	1770	$8.13 \cdot 10^{-9}$
48	20»	1063°	$\perp \{001\}$	Ra	508.00	0.30	1690	$7.14 \cdot 10^{-9}$
49	20»	1063°	$\perp \{010\}$	Ra	460.00	0.35	1315	$4.32 \cdot 10^{-9}$
50	20»	1063°	$\perp \{010\}$	Ra	500.00	0.35	1430	$5.12 \cdot 10^{-9}$
51	20»	1063°	$\neq [100]$	Ra	524.00	0.15	3490	$3.04 \cdot 10^{-8}$
52	20»	1063°	$\neq [100]$	Ra	1217.00	0.35	3510	$3.08 \cdot 10^{-8}$

Standard sample 96.2 mg Ra-glass, specific gravity 2.65. Activity 560.3 count.min⁻¹. Distribution coefficient 1.045.

Fig. 3 shows the values found, represented graphically in the same way as the previous diagrams. The observations are seen in relation to the theoretical curves based on the following values:

$$\begin{array}{lll} \perp \{001\} & D_0 = 5.1 \cdot 10^{-4} & \omega = 24\,300 \text{ cal/ion} \\ \perp \{010\} & D_0 = 2.4 \cdot 10^{-4} & \omega = 24\,000 \text{ cal/ion} \\ \neq [100] & D_0 = 2.0 \cdot 10^{-2} & \omega = 28\,200 \text{ cal/ion} \end{array}$$

Table 4. Diffusion of Ra^{++} in albite.

Expt. no.	Time	T	Cryst. direc.	Tracer	Count min ⁻¹	Cross-section contact area in cm ²	Count cm ⁻² min ⁻¹	D
55	160h	848°	$\perp \{001\}$	Ra	27.4	0.07	390	$4.23 \cdot 10^{-11}$
56	160»	848°	$\perp \{001\}$	Ra	87.6	0.22	395	$4.34 \cdot 10^{-11}$
57	160»	848°	$\perp \{010\}$	Ra	34.3	0.09	375	$3.84 \cdot 10^{-11}$
58	160»	848°	$\perp \{010\}$	Ra	34.7	0.115	310	$2.68 \cdot 10^{-11}$
59	160»	848°	$\neq [100]$	Ra	98.5	0.13	760	$1.77 \cdot 10^{-10}$
60	160»	848°	$\neq [100]$	Ra	110.0	0.10	1100	$3.66 \cdot 10^{-10}$
61	20»	1073°	$\perp \{001\}$	Ra	334.0 300	0.32	939	$2.60 \cdot 10^{-9}$
62	20»	1073°	$\perp \{001\}$	Ra	770.7	0.085	445 45	$1.22 \cdot 10^{-9}$
63	20»	1073°	$\perp \{010\}$	Ra	54.9	0.085	872	$1.95 \cdot 10^{-9}$
64	20»	1073°	$\perp \{010\}$	Ra	170.7	0.210	645	$1.22 \cdot 10^{-9}$
65	20»	1073°	$\neq [100]$	Ra	752.0	0.28	2675	$2.04 \cdot 10^{-8}$
66	20»	1073°	$\neq [100]$	Ra	404.2	0.212	1920	$1.08 \cdot 10^{-8}$

Standard sample 96.2 mg Ra-glass, specific gravity 2.65. Activity 560.3 count.min.⁻¹. Distribution coefficient 1.03.

Fig. 4 shows the value found, represented graphically in the same way as the previous diagrams. The observations are seen in relation to the theoretical curves based on the following values:

$$\begin{array}{lll} \perp \{001\} & D_0 = 4.8 \cdot 10^{-3} & \omega = 31\,000 \text{ cal/ion} \\ \perp \{010\} & D_0 = 1.6 \cdot 10^{-3} & \omega = 29\,800 \text{ cal/ion} \\ \neq [100] & D_0 = 5.0 \cdot 10^{-2} & \omega = 32\,200 \text{ cal/ion} \end{array}$$

Fig. 4. Diffusion of Ra^{++} in albite.

$$\begin{aligned}
 I \perp \{001\}. \quad D &= 4.8 \cdot 10^{-3} e^{-\frac{31000}{RT}} \\
 II \perp \{010\}. \quad D &= 1.6 \cdot 10^{-3} e^{-\frac{29800}{RT}} \\
 III \neq [100]. \quad D &= 5 \cdot 10^{-2} e^{-\frac{32200}{RT}}
 \end{aligned}$$

DISCUSSION

The experiments mentioned above clearly indicate that radium is diffusing more rapidly $\neq [okl]$ than in the two other directions at the temperatures where experiments were performed. This is the case both in microcline and in albite. The activation energy, however, is greater in this direction and at a lower temperature, it seems as if the diffusion would have the same rate along the 3 crystallographic directions. In the case of albite this should be the case at the temperature of about 400°K , and in the case of microcline pertite about 475°K . The empirical formula $D = D_0 e^{-\frac{Q}{RT}}$ gives no real information as to the mechanism of the diffusion processes. It is, however, reasonable to assume that the energy of activation must be higher by diffusion $\neq [100]$ than by diffusion $\perp \{001\}$ and $\perp \{010\}$. At the same time the possibility for a movement in the direction $\neq [100]$ must be considerably greater than in the two other directions.

Glasstone, Laidler, and Eyring⁸ give an equation for diffusion in solid substances under certain conditions. According to this assumption the diffusion constant D_0 may be identified with $\lambda \gamma$. Here λ means the free path for diffusion and γ is the vibration frequency of the considered ion in the direction of diffusion. The fact that the diffusion has the greatest velocity in

the direction where the activation energy has a maximum, seems curious. Similar conditions have, however, been found earlier by Seith⁹ in his studies of selfdiffusion in bismuth. The theoretical interpretation of the phenomenon is not quite clear as yet, and in this paper I will not try to deal with this point. There is, however, another point which seems striking; namely, the fact that radium diffuses more slowly in all directions in albite than in microcline pertite at the temperature intervals investigated. At the same time the activation energy in albite is higher than in microcline pertite. In the case of lead, however, the diffusion coefficient is much smaller in microcline than in albite. The activation energy for lead in albite is, however, much higher than in microcline. It is possible that this is due to the fact that lead easily enters isomorphically into potash feldspar lattice, but not into the albite lattice.

It seems reasonable that the activation energies in microcline pertite are lower than in albite. We must from other crystal investigations expect a higher degree of irreversible disorder in microcline pertite than in albite, and even microscopical investigations show that the albite lamellae in the pertites are clear and homogenous. The microcline parts, however, often seem unclear and filled with microcrystals.

A further question is how the radioactive components are passing from the glassdrop into the crystals. We may assume an exchange of cations in the glass phase and in the crystal phase. Potassium ions may diffuse into the glass and lead ions may diffuse from the glass into the crystal. Barth¹⁰ thinks that oxygen provides a fairly stationary medium in the silicates because of the fact that the volume of oxygen is larger than the volume of the cations. In this stationary oxygen medium he thinks that the cations diffuse. Bengtson¹¹ and Jagitsch¹² have, however, shown by experiments that oxygen diffuses in much the same way as the cations. It seems more likely to me that oxygen as well as metal diffuse either as metal oxide or in an ionised state from the glass phase into the crystal phase, and in the crystal phase the tracer ions and the oxygen ions diffuse independently.

SUMMARY

A method of studying diffusion processes in crystalline silicates is outlined. The diffusion coefficients of Pb and Ra in potash and sodafeldspars are measured at different temperatures. It is shown that the diffusibility depends on the crystallographic directions. The diffusion anisotropy seems to increase with increasing temperature.

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Received May 4, 1949.