IONIC DIFFUSION AND ELECTRICAL CONDUCTIVITY IN QUARTZ

J. Verhoogen, *University of California, Berkeley, California.*

Abstract

The diffusion coefficients of Li^+, Na^+, K^+ parallel to the c-axis of natural quartz crystals in the range 300–500° C. are given by the following expressions:

$$D_{Li} = 6.9 \times 10^{-3} \times e^{-20,500/RT} \text{ cm.}^2/\text{sec.}$$
$$D_{Na} = 3.6 \times 10^{-3} \times e^{-24,000/RT} \text{ cm.}^2/\text{sec.}$$
$$D_K = 0.18 \times e^{-31,700/RT} \text{ cm.}^2/\text{sec.}$$

In the same temperature range the diffusion coefficients of Mg^{++}, Ca^{++}, Fe^{++}, A^{+++} are considerably smaller, below the limit of experimental determination by the present method.

It is suggested that electrical conduction parallel to the c-axis of quartz results from motion of Frenkel oxygen defects. On this hypothesis, the coefficient of self-diffusion of oxygen in quartz at 500° C. is found to be approximately 3×10^{-11} cm.^{2}/sec. It is suggested also that diffusion of foreign univalent ions occurs mainly through vacant oxygen lattice positions. Experimental values are compared with those predicted by the theory of absolute reaction rates.

Table of Contents

Introduction

The minerals and fabric of a rock, either igneous or metamorphic, depend to a large extent on the kinetics of the processes by which the rock is formed. Glassy rocks, for instance, form when the rate of cooling is rapid compared with that of crystallization. Oscillatory zoning in plagioclase presumably testifies to processes that were rapid in comparison with the rate of the exchange reaction between crystal and melt. If minerals A and B in a thermally metamorphosed rock react to produce mineral C, occurrence of C not only indicates that the rock was heated to the equilibrium temperature for the reaction $A + B = C$; it indicates also that the rock was subjected to conditions under which the rate of this reaction

became appreciable as compared to the length of time during which the rock was held under those conditions. This may point to a temperature much higher than the equilibrium temperature, or to operation of other catalytic factors. It is possible, also, that C might form as a metastable phase below the equilibrium temperature, as when cristobalite forms well below its own range of stability. Some knowledge of reaction rates, and of factors which may affect them, is thus essential to correct understanding of the sequence of events recorded in igneous or metamorphic rocks.

The over-all rate of a heterogeneous reaction involving several successive steps is determined essentially by the rate of the slowest step. There is little doubt that in processes involving solids, the rate-determining step, or "bottleneck," is the rate of diffusion of reactants and products in the various solid phases. For instance, the rate of the reaction by which a crystal of quartz is converted to orthoclase, or andalusite is replaced by muscovite, depends mostly on the rate at which the alkali aluminates diffuse through the pre-existing crystal lattice. Knowledge of diffusion rates in solid silicates is thus of fundamental importance. The object of the present paper is to report on some experiments to determine the order of magnitude of the diffusion coefficients of common ions (K^+, Na^+, Li^+, Mg^{++}, Ca^{++}, Al^{+++}) in quartz.

DEFINITION OF DIFFUSION COEFFICIENT

It is customary to define a diffusion coefficient in the following manner: Let a particle with mass m be subjected to a force F arising from a concentration gradient or, as in the case of the present experiments, from an electrical field. Let it be assumed that this particle moves through a solid medium in which it encounters frictional resistance proportional to its velocity v. The equation of motion is then

$$m \frac{dv}{dt} = F - \frac{1}{B} v$$

where the coefficient B is the "mobility" of the particle. If $v = 0$ at time $t = 0$, the solution of this equation is

$$v = FB[1 - e^{-t/Bm}]. \tag{1}$$

The numerical values of m and B are always such that the velocity

reaches an approximately constant value $v = FB$ within a very small fraction of a second. The mobility B may thus be interpreted as the velocity of a particle under unit force.

Now if c is the concentration of diffusing particles (number of particles per unit volume), the flux, or number S of particles flowing across a unit surface in unit time is

$$S = vc = FBc \tag{2}$$

so that B may be found if F, S, and c are known. Where diffusion results from a concentration gradient, it is convenient to use, instead of B, a "diffusion coefficient" D defined as

$$D = BkT \tag{3}$$

when k is Boltzmann's constant, and T is (absolute) temperature. With this definition we have, very simply, that the flux S_x in any arbitrary direction x under a concentration gradient dc/dx is

$$S_x = - D \frac{dc}{dx} \tag{4}$$

(Turner and Verhoogen, 1951, p. 41). D has dimensions cm². sec⁻¹. B, the mobility, has dimensions GM⁻¹ sec.

Diffusion coefficients are known to increase rapidly with temperature, following in general a law of the type

$$D = D_0 e^{-E/RT} \tag{5}$$

where D_0 is independent (or nearly independent) of temperature. E is an experimental "activation energy" for the process of diffusion.

EXPERIMENTAL PROCEDURE

Equation (4) shows that D may be computed if we can measure the flow of particles under a given concentration gradient. The diffusion coefficient of sodium in quartz at 500° C. is, however, of the order of 10^{-10} cm²./sec. If we had a plate of quartz one millimeter thick in contact on one side with sodium chloride, say, the average gradient across the plate would be of the order of 2×10^{23} (since the concentration of sodium in sodium chloride is about 2.2×10^{22} particles per cm.³), and the resultant flux across the plate would be $2 \times 10^{23} \times 10^{-10} = 2 \times 10^{+13}$ particles per cm.² per second, or only 0.07 milligram/day. The actual rate would be much less because not all sodium ions in sodium chloride are free to migrate; the factor c which appears in (4) should really be the number of "free" ions, or the "activity" which is considerably smaller than the concentration. Such small diffusion rates have been measured by using radioactive isotopes, but unfortunately the radioactive isotopes of Li, Al and other geologically important elements have very short half-lives and cannot be

employed for this purpose. It is possible, however, to accelerate the ions appreciably by using an electrical field rather than a concentration gradient, and thus obtain a measurable flow.

The experimental technique is simple (Fig. 1). A thin layer of a nonvolatile salt of the ion under study (e.g., NaCl, LiCl) is spread on a platinum foil resting on a lower massive copper electrode inside a furnace. A plate of quartz 2 or 3 mm. thick and 4 or 5 cm.² in cross-section rests on this layer of salt and is covered in turn by a second platinum foil. A heavy upper copper electrode weighs down on the assemblage to maintain good contact. The two copper electrodes are connected to a D.C.
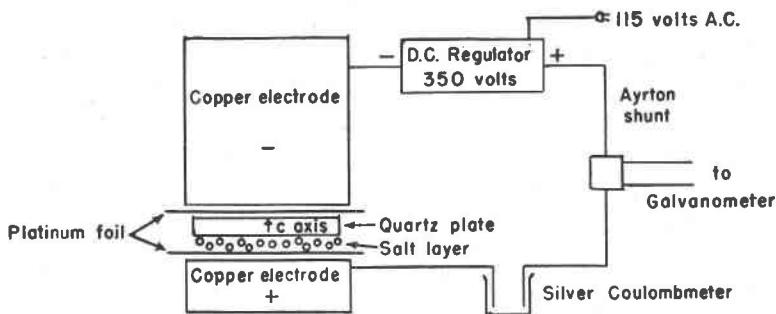

FIG. 1. Schematic drawing of diffusion assembly.

constant voltage supply adjustable in the range 100–350 volts, the upper electrode being the negative one. The metallic positive ions are accelerated towards the upper electrode and move across the quartz plate, carrying a current which is measured by means of a sensitive galvanometer, this current being proportional to the concentration and to the velocity of the diffusing ions, which are collected on the upper platinum foil, usually as a mixture of hydroxide and hydrous carbonates. The total amount transported in a given time may thus be determined by weighing. The total electrical charge which has flowed through the circuit in this same time may be ascertained, if necessary, by inserting a silver coulombmeter in the circuit.

An approximate value of D may be obtained in the following way: Using (3), equation (2) may be written

$$S = D \frac{Fc}{kT}.$$

If an ion carrying a charge ez (z is valency) is placed in a field of intensity dV/dx in the x-direction, the force F in that direction is

$$F = - ez \frac{dV}{dx} \tag{6}$$

the minus sign indicating that a positive ion diffuses towards the negative electrode. As an approximation let us take $dV/dx = -(\Delta V/h)$ where ΔV is the difference in potential and h the thickness of the quartz plate. Then the total number of ions diffusing in time θ across a plate with cross-section s is

$$Q = Ss\theta \tag{7}$$

and

$$D = \frac{kT}{ez} \frac{hQ}{sc\theta\Delta V} \tag{8}$$

from which D may be determined if Q and c are known. Care must be taken to express all quantities in the same units. If e, the electronic charge is expressed in c.g.s.e.u. ($e = 4.8 \times 10^{-10}$), the potential drop ΔV must be expressed in the same units (1 volt $= 1/300$ c.g.s.e.u.). The constant k is 1.38×10^{-16} ergs/deg. The time θ in these experiments was usually of the order of 10 days $= 8.64 \times 10^{5}$ seconds.

Alternatively, D may be determined from the electrical conductivity σ. According to Ohm's law, the current density i (current per unit surface) is

$$i = -\sigma dV/dx. \tag{9}$$

If the current density results from a flux S of particles with charge ez,

$$i = Sez$$

and S, as before, is

$$S = -Bezc \frac{dV}{dx} \tag{10}$$

so that

$$B = \frac{\sigma}{e^2 z^2 c} \qquad D = \frac{\sigma kT}{e^2 z^2 c}. \tag{11}$$

The conductivity σ is usually expressed in ohm^{-1} cm.$^{-1}$, so that, after conversion to electrostatic units

$$D = 5.55 \times 10^{14} \frac{\sigma T}{z^2 c}. \tag{12}$$

The conductivity σ is easily determined for simple geometric shapes from the potential drop ΔV and the total current I flowing through the circuit

$$\sigma = Ih/s\Delta V$$

where σ will be given in ohm^{-1} cm.$^{-1}$ if I is expressed in amps. and ΔV in volts.

Equation (12), of course, is only applicable if it can be ascertained that the conductivity is due entirely to the diffusing ion. This, however, is

rarely the case, for part of the current may be carried by electrons, or by ions of opposite sign diffusing in the opposite direction. Occurrence of such negative carriers appears indeed to be a necessity, for if only positive ions were to diffuse into and through the quartz plate, the plate would soon acquire a very high electrostatic charge. This could be checked by comparing the intensity of the current as it enters or leaves the crystal. The equation of continuity

$$\text{div } i = -\frac{\partial \rho}{\partial t}$$

where ρ is the density of electrical charges shows indeed that the current must decrease in the x-direction if positive space charges are being built up. No differences in current could be detected that could not be traced to leakage through faulty insulation.* Hence, it appears that the crystal plate as a whole maintains electric neutrality during the process of diffusion, which requires a motion of negative charges to balance advancing positive charges. A comparison of the values of Q and of the integral $\int_0^\theta I dt$ (measured with a coulombmeter or by graphical integration) shows that usually no more than about 50% of the current is carried by the diffusing ion. The exact proportion, however, is uncertain because of difficulty in determining exactly the quantity Q. What is collected on the negative electrode is indeed usually found to consist of a mixture of hygroscopic hydroxides and carbonates in various states of hydration (in the case of lithium, for instance, at least three constituents were recognized optically in the deposit); and it is difficult to determine the exact proportion of each of these in a deposit weighing a few milligrams or less. This uncertainty on Q appears to be the main source of error in these experiments.

The question also arises as to whether diffusion occurs through the body of the crystal or through mechanical defects such as invisible cracks, or grain boundaries, or twin planes. The quartz crystals used in these experiments were natural crystals and were certainly not free from defects, as shown by the scatter in observed values of the conductivity of the quartz itself. In general, quartz plates used for diffusion experiments were selected on the basis of their low conductivity, which was interpreted to indicate few mechanical defects. In spite of this, diffusion along cracks could be shown in the case of experiments with silver. Silver ap-

---

* Since the resistance of a quartz plate 2 mm. thick and 5 cm.² in cross-section is about 4×10^8 ohms at 500° C., careful insulation is necessary, particularly where the wires enter the furnace. Also, on account of the extreme resistivity of quartz, it was not found practicable to place guard rings around the quartz plate, as the insulating material between rings and main electrodes could probably be a better conductor than quartz itself.

parently diffuses with extreme rapidity through such cracks which are later found to be lined with a thin deposit of metallic silver. This produces a rapid and very marked increase in conductivity, which soon reaches values typical of conduction in metals. Such, however, was not the case with the other ions, such as K, Li, Na, Mg, etc. The crystal remains perfectly clear after the experiment and the cathodic deposit is usually evenly distributed on the negative electrode, reproducing the outline of the plate. It is thus likely that transport of ions occurred mainly through the lattice itself. In any event, since the measurements were carried out on natural crystals, present results should be applicable to processes of diffusion in real crystals in nature.

EXPERIMENTAL RESULTS

Using for c, the average concentration of the diffusing ion, a value the determination of which will be discussed later, the following results were obtained for the diffusion coefficient at 500° C., for diffusion parallel to the c-axis of quartz.

$$D_{Li} = 1.1 \times 10^{-8} \text{ cm.}^2 \text{ sec.}^{-1}$$
$$D_{Na} = 5.8 \times 10^{-10} \text{ cm.}^2 \text{ sec.}^{-1}$$
$$D_{K} = 2.0 \times 10^{-10} \text{ cm.}^2 \text{ sec.}^{-1}$$

These values are not believed to represent more than the order of magnitude of the diffusion coefficients; numerical values may be in error by a factor of 2 or 3.

To obtain the temperature coefficient of diffusion rates, it was assumed that since c changes only very slowly (due to the small value of the diffusion coefficient), any rapid change in σ with temperature would be due essentially to changes in D itself (see equation 12). It was found that by cooling or heating rapidly (i.e., in a matter of an hour) a quartz plate in which diffusion had been going on at a steady rate for some time (of the order of a few days), the conductivity changed exponentially, i.e., could be represented as a function of temperature by the relation

$$\sigma = \sigma_0 e^{-E/RT}.$$

The value of E appearing in this relation was taken to be the same as that appearing in equation (5), and was determined by measuring the ratio of the conductivities at two different temperatures, provided these two measurements could be carried out within a short interval of time. The following values were obtained, by averaging several determinations

$$E_{Li} = 20,600 \text{ cal./mole}$$
$$E_{Na} = 24,000 \text{ cal./mole}$$
$$E_{K} = 31,700 \text{ cal./mole}$$

with a probable error of ± 1000 calories, approximately. Combining these

results with the values of D at 500°, the following values were obtained in the range 300–500° C.

$$D_{Li} = 6.9 \times 10^{-3} \times e^{-20,600/RT}$$
$$D_{Na} = 3.6 \times 10^{-3} \times e^{-24,000/RT}$$
$$D_{K} = 0.18 \times e^{-31,700/RT}.$$

Tests were also made with Mg^{++}, Ca^{++}, Fe^{++} and Al^{+++}. In the case of Mg, a small amount of magnesium was detected spectroscopically on the negative electrode after a few days, but the amount was too small to be determined with accuracy; hence D_{Mg} is probably less than 10^{-12} at 500° C. The other ions gave completely negative results, and probably hardly diffuse at all. The anomalous case of silver, using silver foil as a source, has been mentioned earlier. Similar tests with gold, platinum, aluminum and copper foils gave no result at all.

Electrical Conductivity of Quartz

In order to throw light on the mechanism of diffusion, experiments were made on the conductivity of quartz in the absence of diffusing ions from an external source. The conductivity of quartz has been investigated by many writers apparently because of its peculiar behavior (for a summary of earlier work see Sosman, 1927, pp. 525–554). It is well known, for instance, that the conductivity parallel to the c-axis is considerably greater than the conductivity along any direction normal to this axis. The c-conductivity at 500° C. was found in our experiments to range from about 5×10^{-10} to 5×10^{-9} ohm^{-1} cm.$^{-1}$, depending on the specimen, whereas Rochow (1938) reports an equatorial conductivity of 2.1×10^{-12} at this same temperature. Rochow states that the equatorial conductivity is essentially electronic, whereas current in the c-direction is carried mainly by ions. Reasons for this difference are not known.

An interesting feature of the c-conductivity is its dependence on time. If a plate of quartz is placed between electrodes and a field applied in the direction of the c-axis, the current flowing through the circuit decreases at first very rapidly, then more slowly. Although the actual rate of decay varies somewhat from one sample to the next, the current after 10 or 15 minutes is commonly less than 1/10 of the current after 1 minute; indeed, the initial rate of decay (that is, during the first minute) is so great that it is difficult to determine experimentally the value of the initial conductivity. Conductivity may be observed to decrease continuously, although more slowly, over periods of many days. [This is in sharp contrast to the behavior observed when foreign ions are made to diffuse through the plate, in which case the conductivity increases slowly with time as more and more ions move into the crystal.] (Fig. 2). If the electric field is removed after a certain time, the quartz slowly regains its initial

conductivity, but if the field is actually reversed, the conductivity reverts almost instantaneously to its initial value or a higher value. Apparently, this is why the conductivity for alternating current is considerably higher than for direct current. If the circuit containing the quartz plate is short-circuited after removal of the field a "recovery," or "relaxation," or "inverse" current is observed to flow, the quartz plate acting somewhat like a storage battery. Joffé (1929) claims that this recovery current equals in magnitude the direct, or charging current; in our own experiments the recovery current was always considerably less than the charging current, although it decays at about the same rate.

The conductivity of quartz depends on temperature according to an exponential law

$$\sigma = \sigma_0 e^{-E/RT}$$

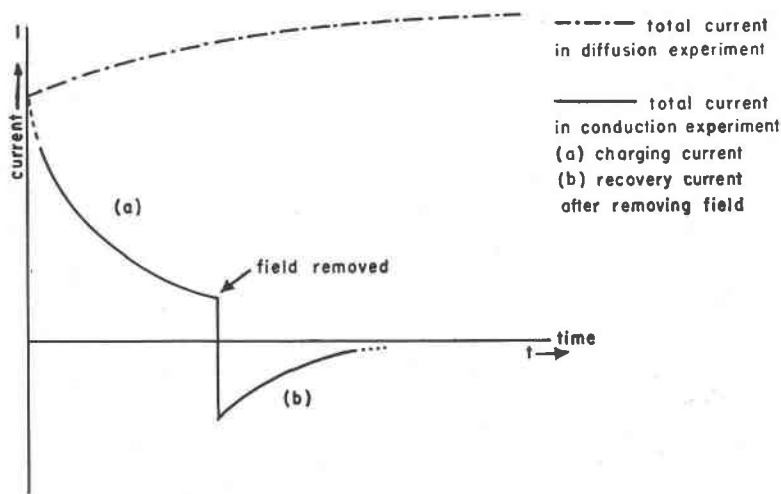where the activation energy is about 23,000 cal. in the range 300–500° C.

FIG. 2. Current-time curves for conduction and for diffusion in quartz.

There is no sudden change in the conductivity at the α-β transition point, although the activation energy seems to increase somewhat above this point. If a specimen is heated slowly to 500° and allowed to cool, the conductivity measured during cooling is less (by a factor of 2 to 3) than the conductivity measured during heating; but this may be due partly to the time dependence of conductivity since the cooling curve is determined after the heating curve. Curie (1889) observed however, that the conductivity may be greatly reduced by preheating the specimen. This effect is presumably similar to annealing, insofar as preheating re-

moves lattice defects due to strain or acquired otherwise during the previous history of the crystal, and which contribute to the conductivity.

Several explanations have been suggested for the time-dependence of axial conductivity. Curie (1889) suggested that it results from water filling channels of molecular size parallel to the c-axis; the conductivity of this water would gradually decrease as more and more of the salts dissolved in it are removed by electrolysis. Warburg and Tegetmeier (1888) suggested that the conductivity is due to ions (mostly Na) present initially as impurities in the quartz lattice; again these foreign ions would be gradually eliminated. There is little doubt that part of the initial con-
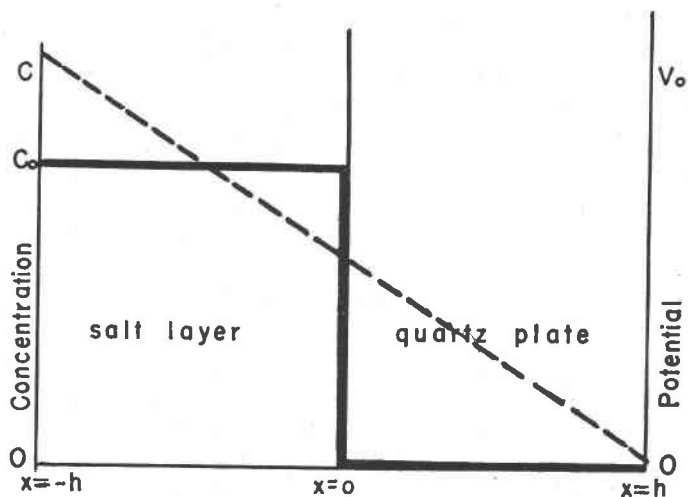

FIG. 3. Initial distribution of potential and concentration in diffusion experiments.

ductivity of quartz may be due to such impurities, for in one of our experiments with a quartz crystal from Arizona, noticeable amounts of boron were collected on the cathode. But such "impurity" theories fail to explain why quartz may regain its initial conductivity merely by standing for a few days.

The same time-dependence of conductivity has been observed for other ionic crystals, such as NaCl, and Beran and Quittner (1930) pointed out that both the rate of decay of the recovery current and the absence of any measurable change in dielectric constant of a crystal during an experiment indicate that the time-dependence of conductivity, or the existence of a recovery current cannot be due only to displacement currents and dielectric polarization. Joffé (1929) and von Seelen (1924) have succeeded in measuring the potential distribution across crystals of quartz and halite respectively, and from the curvature of the potential

curve showed the existence of space charges. In NaCl these are mostly positive charges accumulated on the anode-side of the crystal, whereas in quartz Joffé found practically equivalent amounts of positive and negative charges, the positive charges residing on the half of the crystal plate in contact with negative electrode. It is apparently the gradual building up of these space charges which produces the decrease in the charging current, whereas a redistribution and gradual disappearance of these same charges explains the recovery current. Joffé explained the occurrence of these space charges by assuming dissociation of quartz into units of opposite sign which migrate in opposite directions in the electric field. He was vague as to the nature of these units, although he mentioned briefly (p. 92) that "a deposit of silicon and liberations of oxygen from a normal crystal lattice may be observed." He succeeded in measuring the average density of these positive and negative space charges and found them to be roughly equal, with a value of 2×10^9 electronic charges per cm.³ at 17° C.

MECHANISM OF CONDUCTION AND SELF-DIFFUSION RATE OF OXYGEN

It is now well known that electrical conduction in ionic, or nearly ionic, crystals results essentially from the motion of lattice defects, although electronic conduction may also be present in some cases (e.g., Ag_2S, FeO). The lattice defects usually considered in this connection are either of the Frenkel or Schottky type. In the former type, ions are assumed to move from a lattice to an interstitial position, leaving "holes" behind them; other lattice ions may then be expected to move into these holes, which therefore migrate in a direction opposite to that of the ions themselves. In the Schottky type of defect it is assumed that ions of both signs migrate out of the lattice towards its surface, leaving equivalent numbers of holes of both signs which migrate in opposite directions when an electrical field is applied. If ϵ_F is the energy per ion to form a Frenkel defect, i.e., to move an ion from a lattice to an interstitial position, the number n_F of such interstitial ions in a crystal in equilibrium at temperature T is (Mott, 1948, p. 21)

$$n_F = \gamma \sqrt{N N^1} e^{-\epsilon_F / 2kT}$$

where N is the total number of lattice positions and N^1 is the number of possible interstitial positions. The factor $\frac{1}{2}$ in the exponential arises from the fact that displacement of *one* ion creates *two* defects (an interstitial ion and a hole). The factor γ arises from the change in vibrational frequencies, and hence in free energy, of the atoms and ions surrounding the interstitial ion or the hole; it may be greater or less than 1. The number n_S of Schottky defects, on the other hand, is

$$n_S = \gamma N e^{-\epsilon_S/kT}$$

being the energy to produce such a defect. The factor γ in this case may be of the order of $10^3 - 10^4$ (see also Barrer, 1941, p. 294). Thus if electrical conduction results from motion of Frenkel defects, its temperature coefficient would be of the type $exp[-(\epsilon_F + 2\epsilon_F')/2kT]$ where ϵ_F' is the activation energy for migration of a defect, whereas for conduction by Schottky defects the corresponding term would be $exp[-(\epsilon_S + \epsilon_S')/kT]$ ϵ_S' being the activation energy for migration of a Schottky defect.

As mentioned above, Joffé finds that the average density of charges of one sign in quartz at 17° is 2×10^9 electronic charges per cm.[3] If this corresponds to the density of Frenkel defects for oxygen ions, the corresponding number of interstitial oxygen ions is 1×10^9/cm³. The total number N of oxygen lattice position in one cm³ of quartz is approximately 5.2×10^{22}, so that assuming $\gamma = 1$, $N = N^1$, we find $\epsilon_F = 36,400$ cal./mol. [The same value would obtain if we considered silicon defects.] The activation energy for conduction in quartz is about 23,000 cal. Hence

$$(36{,}400 + 2\epsilon'_F)/2 = 23{,}000$$

and $\epsilon_F' \cong 5,000$ cal./mole. On the other hand, if conduction occurs by Schottky defects we find, for $\gamma = 10^4$, $\epsilon_S = 23,800$ cal., $\epsilon_S' = -800$ cal., which is impossible. These figures are, of course, quite approximate, since an exact calculation would require evaluation of γ for the quartz lattice, which is not available. The suggestion is, however, that conduction occurs by Frenkel defects, which is what one would expect in a lattice with high evaporation energy (hence high ϵ_S) and relatively high compressibility (hence low ϵ_F).

It is impossible to decide from Joffé's experiments whether oxygen, or silicon, or both, move into interstitial positions, but it seems likely that it is oxygen. Removing an oxygen requires breaking 2 O—Si bonds, whereas removing a silicon requires breaking 4. In other cases it is usually the ion with the lesser charge (in this case O^{--}) which moves most readily.

If the hypothesis is accepted that conduction of electricity parallel to the c-axis in quartz results from motion of oxygen ions in one direction and simultaneous displacement of holes (bearing an effective positive change) in the opposite direction, it becomes possible to compute the self-diffusion coefficient of oxygen from the conductivity itself by using equation (12). Joffé's measurements show that the mobility of oxygen ions and oxygen holes is about the same; hence it may be assumed that either one carries half the total current. From the number of defects at 17°, measured by Joffé, the number of such defects at 500° C. is found to be 3.6×10^{18}/cm³. Then

$$D_0 = 5.55 \times 10^{14} \times \frac{\sigma}{2} \times \frac{773}{4 \times 3.6 \times 10^{18}}.$$

Thus for a crystal with an initial conductivity (obtained by extrapolation of the readings after 1 minute) of 2×10^{-9}, the diffusion coefficient of oxygen is 3×10^{-11} cm.²/sec.

MECHANISM OF DIFFUSION

Very simple experiments with a scale model of the quartz lattice and marbles of various sizes indicate that the maximum radius of a rigid sphere capable of moving freely through the lattice is about 0.57 Å; larger ions cannot diffuse without making room for themselves by distortion of the lattice, or availing themselves of preexisting holes. If the diffusing ion makes room for itself by crowding the lattice ions aside, the energy requirements, and hence the diffusion rates, would be very sensitive to ionic size. While this is true to some extent, the fact remains that the large K^+ ion diffuses more rapidly than smaller bivalent or trivalent ones. Hence, foreign ions may diffuse mainly through preexisting holes, such as vacant oxygen lattice positions. Once a foreign ion, say sodium, has occupied a hole, it moves farther under the influence of the electric field or of a concentration gradient by exchanging position with neighboring oxygens which migrate in the opposite direction, thus accounting for the fact that the diffusing ion apparently carries only a fraction of the total current.

Since the oxygen holes are originally distributed uniformly through the crystal, they cannot all become occupied at once. The number of admitted ions and occupied holes will thus increase gradually with time, leading to a gradual increase in conductivity, as observed. (See Fig. 2.) When all the holes are occupied, the conductivity reaches a steady value, which is usually found to occur after a few days. The concentration of diffusing ions then presumably reaches a maximum value of 3.6×10^{18}/cm.³ at 500° C. The values of the diffusion coefficients listed above were obtained by substituting this value and the corresponding value of the steady-state conductivity in equation (12), checking the result by means of (8) to determine the fraction of the total conductivity due to migration of the diffusing ions.

An oxygen hole, formed by removing a negative oxygen ion to an interstitial position, carries an effective positive charge; it would then tend to repel an invading positive ion. This repulsion would increase with increasing charge of the diffusing ion. This may explain why bivalent ions, even of relatively small size (e.g., Mg^{++}) diffuse more slowly than larger univalent ones (e.g., Na^+, K^+).

How the crystal manages to maintain electric neutrality during the process of diffusion is difficult to understand. The charge corresponding with a concentration of 3.6×10^{18} foreign univalent ions per cm.³ would be

sufficient to raise the potential of the capacitance formed by the quartz plate and its metallic electrodes to a value of about 10^{10} volts, which obviously does not happen. It is thus necessary to assume that additional negative charges are also present. These might consist, for instance, of negative oxygen ions in excess over the stoichiometric proportion. Such is the case, for instance, for cuprous oxide which shows a marked increase in conductivity when heated under high partial pressure of oxygen. Electric neutrality in quartz could also be restored by electrons from the external source which become trapped in the crystal structure.

It is interesting to compare experimental values of the diffusion coefficients with values predicted from the theory of absolute reaction rates. According to Eyring's theory [Glasstone, Laidler and Eyring, 1941] the constant D_0 in equation (5) should be given by the relation

$$D_0 = e\lambda^2 \frac{kT}{h} e^{\Delta S/R}$$

where k and h are the Boltzman's and Planck constants, respectively, λ is the average length of a jump, i.e., the distance between successive equilibrium positions of the diffusing particles, and ΔS is the entropy of activation. λ is not likely to be less than the distance between two oxygen sites, which is about 2.6 Å. Substituting this value and the experimental value of D_0 at 500° C., the following values of the entropy of activation are found:

$$\text{for Li } \Delta S = -1.45R$$
$$\text{for Na } \Delta S = -2.1R$$
$$\text{for K } \Delta S = +1.8R.$$

As we have chosen a minimum value for λ, the above values of ΔS are the maxima that are consistent with the experimental values of D_0. It is interesting to notice that the value for Na is such as could have been predicted on the simplest possible hypothesis, namely, that the entropy of activation corresponds merely to a redistribution of degrees of freedom, the diffusing sodium ion exchanging its three vibrational degrees of freedom in the NaCl lattice for one translational degree of freedom in the direction of diffusion. This would correspond to a negative entropy change of about $2R$ at 500° C. This negative value of the entropy of activation indicates also that diffusion of sodium and lithium does not involve any considerable distortion or disordering of the quartz lattice, in agreement with our hypothesis that diffusion occurs through preexisting holes. This, however, is no longer true for potassium: the positive value of the entropy of activation indicates in this case that some disordering does occur, presumably because of the larger size of the potassium ion. This disordering may well occur when oxygen and potassium

ions exchange position, and is consistent with the higher value of the activation energy observed in this case.

GEOLOGIC IMPLICATIONS

To give a more pictorial representation of diffusion rates in quartz, let us assume that potassium ions diffuse from a plane boundary into a quartz crystal under the influence of a concentration gradient. The average distance $\bar{x}$ from the boundary reached by potassium ions after time t is then given by the relation

$$\bar{x}^2 = 2Dt$$

so that, at 500° C., the average distance reached in one million years $(3 \times 10^{13}$ sec.) is

$$\bar{x} = (2 \times 2 \times 10^{-10} \times 3 \times 10^{13})^{1/2} \cong 110 \text{ cm.}$$

which is very small compared to the dimensions of a batholith, say. It should be remembered also that these diffusion coefficients apply to diffusion parallel to the c-axis; diffusion normal to this axis is apparently much slower. Admittedly, in large masses of rocks, diffusion will occur preferentially along crystal boundaries rather than through crystals; yet metasomatic replacement does involve at times penetration into the grains themselves. Present results would indicate very slow rates of metasomatic replacement.

Are the present results at all applicable to processes of metasomatic replacement? The popular view of "clouds of ions" diffusing into rocks and replacing them is, of course, completely inadequate unless these "clouds" happen to be of such composition as to remain electrically neutral; otherwise the diffusion cloud, if it has any appreciable concentration, would involve impossibly large electric potentials. Thus the "cloud" which allegedly transforms great masses of quartz into great masses of orthoclase must contain, in addition to potassium and aluminum ions, a proper number of oxygen ions, as shown already by the simple fact that the chemical formula $3 \text{ SiO}_2 + \text{K}^+ + \text{Al}^{+++}$ does not add up to orthoclase KAlSi_3O_8. The problem of the source of this oxygen does not seem to have been given proper attention. It might be solved by assuming removal of some of the silicon, i.e., $4\text{SiO}_2 + \text{K}^+ + \text{Al}^{+++} = \text{KAlSi}_3\text{O}_8 + \text{Si}^{++++}$; but once again the problem of electric potential in the cloud would present itself. Furthermore, since diffusion rates in quartz seem to be more sensitive to electric charge than to ionic size, diffusion of Si^{++++}, which would be the rate-determining step of the reaction, must be extremely slow. Obviously, diffusion in the solid state does not have the answer to all our problems.

APPENDIX

EQUATIONS OF DIFFUSION IN AN ELECTRICAL FIELD

Let us suppose that a positive ion with valence z diffuses from a layer of salt of thickness h into a quartz plate of equal thickness under the influence of an electrical field (Fig. 3). At time $t=0$, the concentration satisfies the conditions

$$c = c_0 \quad \text{for} \quad -h < x < 0$$
$$c = 0 \quad \text{for} \quad 0 < x < h$$

and may thus be represented by the function

$$c = \frac{c_0}{2} - \frac{2c_0}{\pi}\left[\sin\frac{\pi x}{h} + \frac{1}{3}\sin\frac{3\pi x}{h} + \frac{1}{5}\sin\frac{5\pi x}{h} + \cdots \right]. \tag{1}$$

At time $t=0$, we apply a potential $+V_0$ at $x=-h$, the potential at $x=+h$ being taken as zero. Hence, at $t=0$, $\partial V/\partial x = -(V_0/2h)$; and $V = V_0$ for $x=-h$, $V=0$ for $x=h$ at all times.

1. Let us assume first that only the positive ion moves (no negative carriers). The equations to be satisfied for $o < x < h$ are

(a) The equation of continuity

$$\text{div } S = -\frac{\partial c}{\partial t} \tag{2}$$

where S, the flux in the x-direction, is

$$S = vc \tag{3}$$

the velocity v being given by the relation

$$v = -ezB\frac{\partial V}{\partial x}. \tag{4}$$

(b) Poisson's equation

$$\frac{\partial^2 V}{\partial x^2} = -\frac{4\pi}{\epsilon}ezc \tag{5}$$

where ϵ is the dielectric constant of quartz.

Eliminating S, V, and v leads to the equation

$$c^2 + \frac{\partial c}{\partial x}\left[\int_0^x c\,dx - A \right] = -\beta\frac{\partial c}{\partial t} \tag{6}$$

where

$$A = \frac{\epsilon}{4\pi ez}\left(\frac{\partial V}{\partial x}\right)_{x=0}, \qquad \beta = \frac{\epsilon}{4\pi e^2 z^2 B}.$$

It appears simpler to eliminate c rather than V. The differential equation for the potential V is then

$$\frac{\partial V}{\partial x}\frac{\partial^3 V}{\partial x^3} + \left(\frac{\partial^2 V}{\partial x^2}\right)^2 = \frac{1}{ezB}\frac{\partial^3 V}{\partial x^2 \partial t}. \tag{7}$$

Substituting $y = \partial V/\partial x$, $ezB = 1/\alpha$ the general solution of (7) is found to be

$$F\left[\left(y + \frac{\phi}{\alpha}\right), \left(x + \frac{\psi}{\alpha} + \frac{ty}{\alpha^2} + \frac{t\phi}{\alpha^2}\right)\right] = 0 \tag{8}$$

where F is any arbitrary function of the variables indicated in parentheses, ϕ is an arbitrary function of t only, and $\psi = \int \phi dt$. This function F must satisfy the boundary conditions for V given above, and in addition,

$$-\frac{\epsilon}{4\pi ze}\left(\frac{\partial^2 V}{\partial x^2}\right)_{t=0} \text{ must satisfy (1).}$$

2. It seems hardly worth looking for a suitable form of (8), since condition (5) is not likely to represent conditions accurately. Equation (5) implies indeed an unbalanced concentration of space charges, the crystal acquiring a total charge $\int_0^h ezc_h dx$ which would raise its potential to a very high value. We will certainly be closer to experimental facts if we assume a simultaneous motion of negative charges in the opposite direction at a rate sufficient to maintain electric neutrality. Let us then assume first that there is a detailed balancing of charges everywhere, so that $\partial^2 V/\partial x^2 = 0$ and

$$\frac{\partial V}{\partial x} = -\frac{V_0}{2h}$$

at all times. The equations to be satisfied (2, 3, 4) become very simply

$$\mu \frac{\partial c}{\partial x} = -\frac{\partial c}{\partial t} \tag{9}$$

where

$$\mu = (ezBV_0)/2h. \tag{10}$$

The solution of (9), subject to boundary condition (1), is

$$c = \frac{c_0}{2} - \frac{2c_0}{\pi}\left[\sin\frac{\pi}{h}(x - \mu t) + \frac{1}{3}\sin\frac{3\pi}{h}(x - \mu t) + \cdots\right].$$

To determine B, or D, we consider what happens at $x = h$. The concentration there is

$$c_h = \frac{c_0}{2} - \frac{2c_0}{\pi}\left[\sin\frac{\pi\mu t}{h} + \frac{1}{3}\sin\frac{3\pi\mu t}{h} + \cdots\right] \tag{11}$$

and the total number Q of particles flowing across the plate boundary with cross-section s in time θ is

$$Q = \int_0^\theta s\mu c_h dt. \tag{12}$$

Set $n = \mu\theta/h$, $v = sh$, v being the volume of the crystal. Substituting (11) into (12) and integrating, we obtain

$$\frac{Q}{c_0 v} = \frac{n}{2} - \frac{2}{\pi^2}\left[1 + \frac{1}{3} + \frac{1}{9} + \cdots - \left(\cos n\pi + \frac{1}{9}\cos 3n\pi + \cdots\right)\right].$$

The right-hand member of this equation is given approximately, for large values of n, by the expression $\frac{1}{2}(n-1)$, so that

$$n = \frac{2Q}{c_0 v} + 1.$$

Hence, if Q, c_0 and v are known, n may be computed. Since $n = \mu\theta/h$, $\mu = ezBV_0/2h$, we obtain finally

$$D = \frac{2nkT}{ezV_0\theta} \tag{13}$$

from which D may be calculated. A difficulty arises, however, in the determination of c_0. c_0 is not necessarily the total initial concentration of positive ions in the salt; it is the concentration of free ions, i.e., of ions which are not so tightly held in the lattice that they cannot move. c_0 might be taken, for instance, as the number of metallic ions which would participate in electrical conduction in the salt itself. As this number cannot be evaluated accurately at 500° C. for any of the salts used in these experiments, there is nothing to gain by using the exact relation (13) rather than the approximate method (also assuming $\partial V/\partial x =$ constant) outlined previously.

3. Finally, we might attempt a more exact solution by considering that there is not necessarily a detailed balancing of charges at every point in the crystal although its total charge should remain zero. This implies two different carriers (the positive diffusing ion and a negative one) with valencies z_1, z_2 and concentrations c_1, c_2, respectively. Poisson's equation is then

$$\frac{\partial^2 V}{\partial x^2} = -\frac{4\pi}{\epsilon}e(z_1 c_1 - z_2 c_2) \tag{14}$$

subject to the condition

$$\int_0^h \frac{\partial^2 V}{\partial x^2}\,dx = 0 \tag{15}$$

expressing neutrality as a whole. The equations of continuity for each carrier are

$$\left.\begin{aligned}
ez_1 B_1 \frac{\partial V}{\partial x}\frac{\partial c_1}{\partial x} + c_1 ez_1 B_1 \frac{\partial^2 V}{\partial x^2} &= \frac{\partial c_1}{\partial t} \\
ez_2 B_2 \frac{\partial V}{\partial x}\frac{\partial c_2}{\partial x} + c_2 ez_2 B_2 \frac{\partial^2 V}{\partial x^2} &= \frac{\partial c_2}{\partial t}
\end{aligned}\right\} \tag{16}$$

Let us consider the steady state in which the current remains constant, and in which presumably

$$\frac{\partial c_1}{\partial t} = \frac{\partial c_2}{\partial t} = 0.$$

This state is usually reached after a few days. Eliminating $\partial V/\partial x$ in equations (16), we get

$$- c_1 \frac{\partial c_2/\partial x}{\partial c_1/\partial x} \frac{\partial^2 V}{\partial x^2} + c_2 \frac{\partial^2 V}{\partial x^2} = 0$$

and since we assume $\partial^2 V/\partial x^2 \neq 0$ locally

$$\frac{1}{c_2} \frac{\partial c_2}{\partial x} = \frac{1}{c_1} \frac{\partial c_1}{\partial x}$$

which together with (14) and (15) leads to $z_1 c_1 = z_2 c_2$, $\partial^2 V/\partial x^2 = 0$ everywhere. This is contrary to our assumption, and we must conclude therefrom that either there is detailed balancing everywhere, or that a steady state cannot be reached. As it appears experimentally that a very close approach to a steady state may be reached after a few days, $\partial^2 V/\partial x^2$ can never be very large, and may therefore be neglected. We revert thus to the previous case.

REFERENCES

BARRER, R. M. (1941), Diffusion in and through solids. Cambridge University Press.

BERAN, O., AND QUITTNER, F. (1930), Die Feldstärkeabhängigkeit von Gegenspannung und wahren Leitvermögen in Ionenkristallen: *Zeits. für Physik*, **64**, 760–776.

CURIE, P. (1889), Recherches sur la conductibilité des corps cristallisés: *Ann. Chimie Phys.*, ser. 6, **18**, 202–255.

GLASSTONE, S., LAIDLER, K. J., AND EYRING, H. (1941), The theory of rate processes. McGraw-Hill, New York.

JOFFÉ, A. F. (1928), The Physics of Crystals, McGraw-Hill Book Co., New York.

MOTT, N. F., AND GURNEY, R. W. (1948), Electronic Processes in Ionic Crystals, Oxford, Clarendon Press.

ROCHOW, E. G. (1938), Electrical conduction in quartz, periclase and corundum at low field strengths: *Journ. Appl. Physics*, **9**, 664–669.

SOSMAN, R. B. (1927), The Properties of Silica, Chemical Catalog Co., New York.

TURNER, F. J., AND VERHOOGEN, J. (1951), Igneous and Metamorphic Petrology, McGraw-Hill, New York.

VON SEELEN, D. (1924), Ueber die elektrische Leitfähigkeit des Steinsalzkristalles: *Zeits. für Physik*, **29**, 125–140.

WARBURG, E., AND TEGETMEIER, F. (1888), Ueber die elektrolytische Leitung der Bergkrystalls: *Ann. d. Physik u. Chemie*, **35**, 455–467.