THE RATIONAL AND GEOLOGICAL ASPECTS
OF SOLID DIFFUSION

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ABSTRACT

The difficulty of applying a strictly quantitative approach to geological problems is appreciated, yet a rational mathematical treatment of diffusion in minerals is available and of prime assistance in realizing the geological limitations of this mechanism.

Theoretical calculations of the activation energies needed for direct interchange, interstitial, and vacancy diffusion in f.c.c. copper compared to the empirical activation energy determined from self diffusion experiments in copper indicate the prime importance of the vacancy mechanism of diffusion. Calculated and experimentally determined activation energies of diffusion in sodium chloride further strengthen the efficacy of the vacancy mechanism. Activation energies for diffusion of specific solutes in complex silicate minerals can be determined by diffusion experiments, but only a few values are known. Nevertheless, it is known that vapor pressure will greatly increase diffusion rates in ionic bonded minerals, e.g. the diffusion rate of Na\textsuperscript{22} in Yule marble is increased about 10\textsuperscript{6} times at 400° C. and ~300 bars over the diffusivity constant at the same temperature and at 1 bar.

With such quantitative information available, it is evident that the distances over which true solid diffusion can be significant are relatively short, rarely more than 5 to 10 cm. Even so, transport of substances by "trunk lines" over considerably greater distances may be explained by more rapid movement through rock openings, along fracture zones, around mineral grains and finally into crystals through flaws and breaks. Examples are given of the role of diffusion in such specific examples as rate of crystal growth, metamorphism, and metasomatic alteration and replacement.

INTRODUCTION

There has been much disagreement among Earth scientists pertaining to the degree of importance of the mechanism of diffusion in geological and mineralogical processes. The views expressed range from those in which diffusion is stated to be virtually ineffective to those in which diffusion is believed to be the panacea of many geological problems (Perrin & Roubault, 1949). Yet a wealth of experimental information has been obtained by metallurgists on specific diffusion rates and diffusion mechanisms for many metal pairs (Barrer, 1941; Jost, 1952; Mehl, 1936; and Seitz, 1951), including self diffusion measurements of similar pairs (Mapother & Maurer, 1948, and Seitz & Keil, 1933). The results of these studies have not been entirely ignored by geologists; in fact, these results are often cited (Bowen, 1921, and Gilluly, 1948)
by them as evidence of the noneffectiveness of the role of diffusion in certain geological processes. Others, nevertheless, have raised valid objections such as diffusion of ions or atoms in ionic-bonded minerals under geological conditions may take place at rates that are not strictly comparable to rates determined in laboratory investigations on relatively perfect, rather pure, metal crystals at one atmosphere. Of course, a few measurements of diffusion coefficients of some ions or atoms in ionic (and even covalent) bonded minerals have been determined to have empirical values rather comparable to diffusion coefficients and activation energies determined for metals (Fyfe, Turner & Verhoogen, 1958). Even so, the influence of many factors such as the presence of mineralizers of high vapor pressure, lineage structure, grain boundary diffusion, and mass movement of solute material along joints and fractures in rocks and minerals, all might contribute to greatly increased mobility and diffusion rates.

It is suggested, therefore, that the quantitative laboratory approach developed for the most part by the metallurgists when tempered with a knowledge of the geological factors might provide a better understanding of the extent and importance of the geologic role of diffusion. The purpose of this paper, therefore, is to set forth the basic principles of the former as most geologists consider themselves to be qualified in the latter. Nevertheless, some discussion about the influence of the geological factors upon the effectiveness of diffusion is also included.

**Diffusion fundamentals and factors**

**Definition:** Diffusion may be defined as the process by which, under the influence of a chemical potential gradient, atoms, molecules, or ions move from one position to another within a solvent phase. When the phase is a gas, a liquid, or a solid, the diffusion process is more closely defined by the modifying adjectives gaseous, liquid, or solid, respectively. The "driving force" of diffusion is, of course, energy. This is determined by the chemical potential or activity of the solute atoms, a property that may vary in different solvents. Chemical potential, therefore, is specifically the driving force of diffusion.

**Mathematical treatment:** Diffusion rates can be expressed quantitatively by use of Fick's First and Second Laws. Fick (1855) placed diffusion on a rational mathematical basis when he applied by direct analogy the equations pertaining to heat conduction derived by Fourier (1822) many years before to the similar process of diffusion. Even so, the First Law is readily derived by rate theory or statistical mechanics as follows: assume a concentration \(C_A\) of solute atoms at site \(A\) to be equal to the number of atoms \(N_A\) per unit volume \(d \cdot A\) of thickness
(d) and cross-sectional area (A). In juxta-position at site B, therefore, the concentration is $N_B/d \cdot A$. If the number of times an atom of $N_A$ moves in a direction normal to the cross-sectional area (A) per second is $f_A$, and the number of times an atom of $N_B$ moves in the same $\pm x$ direction is $f_B$, then the probability of an atom moving to the right ($+x$) is $f_A/2$ and to the left ($-x$) is $f_B/2$. The net transport of material or solute atoms ($dm$) per unit time ($dt$) that passes through the cross-sectional area $A$ is therefore:

$$\frac{dm}{dt} = N_A \cdot f_A/2 - N_B \cdot f_B/2 \tag{1}$$

As $N_A = C_A \cdot d \cdot A$ and $N_B = C_B \cdot d \cdot A$,
then, $$\frac{dm}{dt} = C_A \cdot d \cdot A \cdot f_A/2 - C_B \cdot d \cdot A \cdot f_B/2 = A \cdot d \cdot (C_A \cdot f_A - C_B \cdot f_B)/2$$

Based on experimental results of diffusion measurements and the definition of diffusion, the assumption should be made that $f_A \neq f(c)$, where $c$ = concentration, and $f_x$ is the jump frequency in the $\pm x$ direction at the interface.

Then $f_0 = f_A = f_B$, where there is no change or movement of the interface boundary,
and $$\frac{dm}{dt} = A \cdot d \cdot f_0/2 \times (C_A - C_B), \text{ but } C_B = C_A - \partial c/\partial x \cdot d$$

Therefore, $$\frac{dm}{dt} = -A \cdot d^2 \cdot f_0/2 \cdot \partial c/\partial x \tag{2}$$

Let the constant $d^2 \cdot f_0/2 = D$ (diffusion coefficient)
then $$\frac{dm}{dt} = -D \cdot A \cdot \partial c/\partial x \text{ (assuming that } D \neq f(c) \tag{3}$$

Equation [3] is Fick's first law. By a similar derivation, his second law $\partial c/\partial t = D \cdot (\partial^2 c/\partial^2 x)$, can be obtained. It is from these two basic equations that the general solutions are obtained for the various boundary conditions that exist in the experimental determinations of the diffusion coefficients. Of particular aid in setting-up these general solutions are Carshaw & Jaeger (1959) and Crank (1956). Two of the most common examples that have been used in geological studies for unidirectional diffusion for (a), the semi-infinite case and, (b) the finite (thin source of solute) case are given by Garrels, et al. (1949) and Jensen (1952) respectively.

In order that the units in equation [3] agree, $D$ must be expressed in units of area/time, usually cm.²/sec. The diffusion coefficient ($D$) therefore is the amount of solute material per unit time ($dm/dt$) that diffuses through a unit cross-sectional area (A) under a unit concentration gradient ($-\partial c/\partial x$). $D$ values obtained from the study of diffusion in metals generally vary from about $10^{-5}$ cm.²/sec. at temperatures in excess of $1000^\circ$ C. to even less than $10^{-20}$ cm.²/sec. at temperatures as high as even a few hundred degrees C. The diffusion rate of Na in
quartz at 500° C. is $5.8 \times 10^{-10}$ cm$^2$/sec. (Veerhogen, 1952), of Na$^{22}$ in microperthite is approximately $10^{-11}$ to $10^{-12}$ cm$^2$/sec. at 550° C. (Jensen, 1952). The diffusion coefficient of Cu$^{64}$ in steely chalcocite from Kennecott, Alaska, has been determined at temperatures above and below the approximate disordering temperature of 105° C. At 130° C., $D \sim 10^{-8}$ cm$^2$/sec., while at 30° C., $D \sim 10^{-10}$ cm$^2$/sec. (Jensen, 1951). A summary of experimental diffusion rates in silicates, as few as they are, is given by Fyfe, et al. (1958, p. 63).

In answer to a question that is often asked, viz., how far will a particular substance diffuse through a given rock or mineral, it should now be evident that the diffusion coefficient indicates only the amount of material that passes through a given cross-sectional area per unit time. The distance of diffusion is indicated by the concentration curve extending with a negative slope from the interface diffusion plane. Theoretically, therefore, there is a probability that at least one diffusion atom may have travelled an infinite distance from the initial plane!

It would certainly be helpful, however, to have a better method of expressing diffusion distances. One might think that a suitable method would be similar to the means by which the rate of radioactive decay is expressed, i.e., the half-life of a radiogenic nuclide. For diffusion, the "half-thickness" would express the distance of diffusion from an interface where the concentration is one-half of the initial concentration. As diffusion curves are not always simple similar exponential curves, this technique is not the panacea it may first appear to be nor is it any quantitative substitute for the rationality of the diffusion coefficient.

**The effect of temperature.** The role of temperature in mineralogy as a source of energy has been dealt with by Buerger (1948). Its effect on diffusion rates is of interest, not only because of the increase in diffusion rates of ions with increase in temperature, but also because of the effect on diffusion rates of structural transformations which are, of course, also functions of temperature.

The simple concept of the behaviour of an atom is that it tends to oscillate about its equilibrium position with a frequency that is determined by its mass and the bond strengths between neighbouring atoms. When the atom receives energy, as in the form of heat, its frequency does not change significantly but the magnitude of its oscillations increases. If the magnitude becomes great enough to exceed the bond strengths or "break" the bonds holding the atom in place, the atom may "jump" to a new position. The energy that it must overcome in order to accomplish this is known as the *activation energy*.

It is common to represent this activation energy graphically by a curve of varying amplitude showing energy sumps, or atomic equilibrium
locations, and energy peaks of height proportional to the activation energy. Less energy is required for an edge ion to break its bonds than an adjacent surface atom. Movement of interior ions requires even more energy. If the energy barrier is represented by a value of \( \xi \) cal./atom, the probability that the atom will reach the activation energy is proportional to the probability function \( e^{-\frac{\xi}{kT}} \) where \( e \) is the natural logarithm, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature.

If \( e^{-\frac{\xi}{kT}} \) is the probability that \( \xi \) will be reached during one oscillation, then the probability per unit time is \( P = f \cdot e^{-\frac{\xi}{kT}} \) where \( f \) is the vibrational frequency. Dushman & Langmuir (1922) have proposed that the diffusion coefficient is approximately equal to the product of the probability per unit time that an atom will jump (\( P \)) and the jump distance squared (\( \delta^2 \)), or:

\[
D = P \cdot \delta^2
\]

therefore,

\[
D = \delta^2 \cdot f \cdot e^{-\frac{\xi}{kT}} \quad [4]
\]

Since the oscillation frequency and the jump distance are fairly independent of temperature for a given substance, a constant (\( D_0 \)) is introduced, and:

\[
D = D_0 \cdot e^{-\frac{\xi}{kT}} \quad [5]
\]

If both \( \xi \) and \( kT \) are multiplied by Avogadro's number (\( N_0 \)); \( k \cdot N_0 \) is the gas constant (\( R \)), and \( N_0 \cdot \xi \) is the activation energy (\( Q \)) measured in cal./mole, thus:

\[
D = D_0 \cdot e^{-\frac{Q}{RT}} \quad [6]
\]

This equation has proven to be fairly accurate when checked with experimental diffusion results that are limited to the temperature ranges of a crystal structure that is undergoing very slow disordering rates, but it has been found that the value of \( D_0 \) does vary. This should not be too surprising as it was assumed that it did not vary with temperature and it is common knowledge that \( \delta \), the jump distance; usually increases with temperature.

The value of equation [6], however, lies in its usefulness for the experimental determination of the activation energy of a particular species of solute atoms in a given solvent system over a given temperature range. This is done by first determining experimentally the diffusion coefficients at, at least, two different temperatures and preferably at several intermediate temperatures for improved precision. Therefore,
if $D_2$ and $D_1$ are the two diffusion coefficients determined at temperatures $T_2$ and $T_1$ respectively, it follows that:

$$D_2 = D_0 \cdot e^{-Q/R T_2} \text{ and } D_1 = D_0 \cdot e^{-Q/R T_1} \quad [7]$$

therefore, \( \ln D_2 = \ln D_0 - Q/R T_2 \quad [8] \)

and \( \ln D_1 = \ln D_0 - Q/R T_1 \quad [9] \)

Subtracting [9] from [8]:

$$\ln D_2 - \ln D_1 = Q/R (1/T_1 - 1/T_2) \quad [10]$$

therefore, $$Q/R = (\ln D_2 - \ln D_1)/(1/T_1 - 1/T_2) \quad [11]$$

which is the slope of the line shown in figure 1. If, therefore, the slope of the line is determined from the diffusion experiments, where the logarithms of diffusion coefficients are plotted versus the reciprocals of the absolute temperatures, the activation energy expressed in calories/mole is:

$$Q = 2.302 \times R \times \text{slope} = 4.583 \times \text{slope} \quad [12]$$

The effect of second order transformations on diffusion coefficients may now be considered. If the diffusion rates of a solute, such as sodium, were measured in a solvent such as $\alpha$ quartz at various temperatures and the logarithms of the diffusion coefficients were plotted.
versus the reciprocal of the given temperatures on semi-logarithm paper, the result should be approximately a straight line as previously explained. If, however, the line was extended with the same slope to temperatures over 573° C., it would be in error. Sodium ions tend to diffuse through β quartz at a higher rate due to the more open structure, and this sudden increase in diffusion would take place at the transformation temperature of about 573° C. In order to determine the activation energy of Na in β quartz, two or more diffusion experiments would have to be made at temperatures over 573° C. The resulting curve would probably be similar to that shown in figure 2. Presumably, the

Fig. 2. Variation of diffusion coefficients and activation energies for α and β quartz.

slope of the two fairly straight lines would be different as the energy of activation of sodium in β quartz would be very likely less than that in α quartz.

Figure 3 exhibits the relationships of diffusion coefficients, for different structural transformations, when they are plotted versus the reciprocal of temperature. The left side of the figure is from Buerger’s work (1948). The log $D$ versus $\frac{1}{T}$ curve for a disordering transformation is based upon results obtained by myself (1951) on the investigation
DISPLACIVE TRANSFORMATION

SECOND ORDER TRANSFORMATION

Fig. 3. Effect of structural transformations on diffusion rates and activation energy.

of diffusion rates of copper (Cu$^{64}$) in high and low temperature structural modifications of chalcocite. The log $D$ versus $1/T$ diffusion curves shown on this figure should serve as a warning against attempts to determine the energy of activation of a particular system when based on only two diffusion runs at widely different temperatures, especially so when all the structural transformations of a mineral are not known. This is particularly true of the feldspar minerals.

Mechanism of diffusion. The relative importance of grain surface, boundary, and volume (solid) diffusion rates is of considerable interest.
Grain boundary and surface diffusion would normally be expected by a priori reasoning to be rather significant when compared to diffusion through a solid. This has been found to be true in the study of diffusion of thorium along tungsten filament wires (Langmuir, 1934). In this case, surface diffusion was found to be more rapid than grain boundary diffusion and much more rapid than volume diffusion.

On the other hand, some investigators (Seith & Keil, 1933) have discovered that grain boundary diffusion in metals is quite negligible, especially at high temperatures. This is presumably true of sulfide minerals and several ionic bonded minerals; i.e., at high temperatures, grain volume diffusion seems to be of primary importance, whereas at low temperatures, grain surface and boundary diffusion rates are much more significant because of the greatly decreased rate of solid diffusion at the lower temperatures.

This effect can be determined by diffusing a solute through pressed tablets which are composed of grains, or crystals, of a given size; in this way, the abundance of grain surfaces and boundaries can be varied from one tablet to another by varying the grain size of different specimens. Identical diffusion experiments can then be performed on the tablets and the effect of grain boundaries and surface area can be ascertained. The importance of solid diffusion in geologic phenomena, nevertheless, ultimately depends on the rate of grain volume diffusion, or true solid diffusion, in order to have a crystal of one composition changed to a crystal of another composition by addition and deletion of ions.

Solid diffusion is usually broken down into three basic mechanisms, especially in the case of metals. These are interstitial diffusion, diffusion by direct interchange, and the so-called vacancy diffusion mechanism. These three mechanisms are shown diagrammatically in figure 4.

Interstitial diffusion takes place by movement of ions through space surrounded by normal atomic sites. This is a more common process in the case of a small atom such as carbon or aluminum diffusion through a crystal structure made up of relatively larger atoms such as iron or copper respectively. It is very likely an important process for diffusion of many cations through ionic and covalent bonded minerals in which the anion is composed of the relatively large oxygen or sulfur atoms that effectively determine the volume of the mineral.

A series of calculations have been made by several investigators (Huntington, 1942; Huntington & Seitz, 1942, 1949, and Zener, 1950) on the energy requirements needed for the different diffusion mechanisms in the case of self diffusion of metallic f.c.c. copper. They determined that the activation energy needed to cause a copper atom to
DIRECT INTERCHANGE

PAIR

CYCLIC (RING)

INTERSTITIAL DIFFUSION

VACANCY DIFFUSION

MECHANISM OF DIFFUSION

Fig. 4. Diagrammatic examples of various mechanisms of diffusion.
jump from its equilibrium site to an interstitial position (known as a "Frankel defect") is approximately 238,000 cal./mole, however, the energy needed for a copper atom to move from one interstitial position to another is only about 11,500 cal./mole.*

Diffusion by direct interchange may occur by the simultaneous exchange of position of two atoms, which is known as pair interchange, or it may occur by a cyclic interchange of three, four, or more atoms. This has been called ring diffusion (Zener, 1950), but a more descriptive term, "cyclic," was proposed by a mineralogist more than thirty years ago (Buerger, 1934). The energy of activation needed in the copper system for pair interchange is approximately 120,000 cal./mole. For cyclic interchange of four copper atoms, it is lowered to a value of about 91,000 cal./mole. In order to have a direct interchange of two atoms, the crystal structure would need to be strongly distorted during the interchange. Because of this "space problem," the mechanism is not accepted with much favor; however, the cyclic type of interchange need not require as much distortion of the crystal structure. Nevertheless, the probability of four atoms moving in the correct directions at a given instant is rare. Possibly the best reason for belief in the ineffectiveness of diffusion by direct interchange is the so-called Kirkendall effect; i.e., the movement of the diffusion interface boundary. By various techniques in several diffusion experiments (da Silva & Mehl, 1951, and Smigelskas et al., 1947) with metals, it has been determined that movement of the interface boundary actually occurs. It is explained by more rapid diffusion of material across the interface in one direction than diffusion of material in the opposite direction. Diffusion, therefore, by direct interchange cannot account for movement of fiducial markers. Even though Smigelskas & Kirkendall (1947) were very successful in demonstrating this effect and measuring it very precisely, it was first noticed by Pfeil (1929) at which time he demonstrated that after a layer of iron oxide had formed on iron or steel, further oxidation occurred not by oxygen diffusing through the rust but by iron diffusing through the rust to form another layer of ferric oxide. It seems quite clear that some questions pertaining to the mechanism of geologic replacement could be elucidated by further similar problems. Incidentally, Pfeil's early work has been done more elaborately with other forms of iron oxide with the results (Himmel et al., 1953) that both iron and oxygen move but at specific rates for specific systems.

*In the metallurgical literature, the activation energies for these mechanisms are expressed in eV (electron-volts). Here, they have been converted to energies expressed in calories/mole. (eV = 1.602 × 10⁻¹⁹ joules/4.184 joules/cal. × 6.025 × 10²³ atoms/mole = 23.1 × k.cal./mole)
The third mechanism, vacancy diffusion, takes place by an atom moving to a vacant site and thereby creating a vacancy in the site previously occupied. In the case of copper, once again, the activation energy required for a copper atom to move to a vacant site is about 23,100 cal./mole. The energy needed to create a vacancy within the copper structure has already been given as having a value of 288,000 cal./mole; however, the energy needed to cause an atom to move on the surface of the crystal and form a vacancy there (known as a "Schottky defect") is much less; it is of the order of 41,600 cal./mole. Through thermodynamic reasoning, furthermore, it is known that any substance has a finite number of vacant atomic sites at any temperature above absolute because of the increase in entropy that results from the disorder that the vacancies introduce. The number of vacant sites, for example, in a sodium chloride crystal is about one per cent of the total sites at a temperature near 800 degrees centigrade (Mehl, 1936), just a few degrees below its melting temperature. In copper, at its melting temperature of 1356° C., it is estimated by approximate calculations (Smigelskas & Kirkendall, 1947) that the proportion of vacancies with respect to the total number of sites available for vacancies may be about 0.1 per cent.

Structural inhomogeneities known as dislocations may very well account for many of these vacant sites. In any regard, however, they are thought to be of great importance in further enhancing the mechanism of vacancy diffusion in metals and also in specific structural types of ionic bonded minerals.

The importance of determining the energy requirements of these different mechanisms is significant because the activation energy determined experimentally from self diffusion studies of metallic copper, including very careful measurements on single crystals, is about 48,000 cal./mole. Apparently, therefore, vacancy diffusion is the favored mechanism of self diffusion in f.c.c. metallic copper. It is, of course, possible that the other mechanisms occur but to a much lesser extent.

Of primary interest to those of the geologic profession are similar calculations that have been determined for ionic bonded substances, the alkali halides. The computed energies of activation for the various mechanisms of diffusion of Na in NaCl as summarized by Sietz (1951) are given below.

Computed:

1. Energy needed to produce a pair of positive- and negative-ion vacancies: (by moving a positive and a negative ion to the surface of the crystal): 43,100 cal./mole
2. Energy needed to move a Na⁺ ion vacancy into an adjacent vacant Cl⁻ site: 11,800 cal./mole
3. Energy needed to move a Cl⁻ ion vacancy into an adjacent vacant Na⁺ site: 12,900 cal./mole
(4) Energy needed to move a vacant Cl⁻ ion site that is adjacent to a pair of Na⁺ and Cl⁻ (neutral charge on vacancy pair) ion vacancies: 8,800 cal./mole
(5) Energy needed to force an ion into an interstitial site and create a vacancy ~65,000 cal./mole

In comparison, experimental values of the activation energy of self diffusion of Na in NaCl have been determined using Na²⁴ as a tracer. In addition, further insight on the prevalent mechanisms of diffusion has been provided by adding given small amounts of the halides of a divalent metal; e.g. SrCl₂, which increases the density of vacant Na⁺ sites in order to maintain electric neutrality. The following values have therefore been determined experimentally (Mapother, et al., 1948 and 1950).

Experimentally determined:

(1) Energy needed to produce a pair of positive- and negative-ion vacancies 48,500 cal./mole
(2) Energy needed to cause migration of a Na⁺ vacancy 18,500 cal./mole

The comparison of computed values with the experimentally determined values indicates similarities. As the NaCl already contains vacancies, a comparatively large additional energy requirement, beyond the energy needed for mobility of Na⁺, is not wholly needed to create vacancies.

The probable mechanisms of solid diffusion in silicate minerals, which is really of the utmost geologic significance, differ from the above mentioned methods in very basic manners even though the energy requirements are very likely of the similar order of tens of k cal./mole. Silicates are composed of specific structures or networks based not only upon various arrangements of the silica tetrahedrons but also upon the number of oxygen atoms of one tetrahedron that are shared with adjacent tetrahedrons. The result is a structural framework, formed by the tetrahedrons, with cations located in the larger openings or “cages” of the framework. When the structure receives energy, in the form of temperature, it generally tends to expand and the atoms are then more capable of migrating or diffusing from one open space or cage to another. Basically, this is an interstitial type of diffusion but it might be more descriptive to refer to the mechanism as interstitial diffusion through a network, or interstitial network diffusion.

Interstitial diffusion is also probable in sulfide and oxide minerals. In fact, diffusion seems to be the most reasonable process by which certain types of replacement occur; for example, during replacement of one sulfide by another. In discussing the mechanism of replacement Buerger (1948) has said, “Lindgren long ago pointed out that replacement occurs on approximately a volume-by-volume basis. While the
field evidence for this has been obvious, the mechanism for accomplishing it has been obscure. Diffusion suggests the mechanism. There is a tendency on the part of crystals to have their volumes determined by their largest atoms. Thus, the volumes of the rock minerals are dominated by their oxygen atoms and the volumes of the sulfides are dominated by the packing of the sulfur atoms. Replacement is, therefore, substantially a matter of the diffusion of new metals into the volumes dominated by oxygen or sulfur atoms. Thus, diffusion supplies a mechanism for approximately maintaining volume during replacement."

Further corroborating support of this mechanism has been given by studies (Jensen, 1957) which indicate that the $\text{S}^{32}/\text{S}^{34}$ composition of host sulfides is identical with the $\text{S}^{32}/\text{S}^{34}$ composition of the replacing sulfide.

**Driving force for diffusion.** An examination of equation (3) indicates that chemical potential of diffusing ions in a solvent is the driving force that causes net transport of solute atoms from one position to another. A specific example, has been cited by Darken (1949) to indicate that chemical potential makes up the driving force of diffusion. Darken investigated the diffusion of carbon in two specimens of austenite iron which were joined together along a planar contact. One specimen contained 3.80% Si and 0.48% C; the second specimen contained 0.05% Si and 0.44% C as shown in figure 5. If the concentration gradient is the sole driving force, one would expect the carbon concentration to approach the concentration as shown by the dashed line at a given time during diffusion and remain similar to this concentration line during continued diffusion but, of course, gradually approach a zero slope. Actually, the concentration, after a diffusion time of days, had the discontinuity in values as shown by the diagram. The explanation for this is that the thermodynamic activity of carbon is increased in the presence of silicon. In the experiment, therefore, there was a greater
probability of carbon moving in the $+x$ direction than in the $-x$ direction, resulting of course in a net movement to the right. Is it possible, therefore, that diffusion could actually produce zoned crystals?

The thermodynamic activity factor mentioned is essentially the same as chemical potential. The force ($f$) that acts upon an impurity or solute atom in a solvent system causing the solute to move in a direction $+x$ can be expressed as:

$$f = - \text{potential gradient} = - \frac{\partial \mu}{\partial x} \cdot \frac{1}{L_0}$$

where $\mu$ is chemical potential, $(- \frac{\partial \mu}{\partial x})$ is the molar chemical potential gradient of the solute atom along the $-x$ direction, and $L_0$ is the Loschmidt Number or the number of molecules per unit volume at $0^\circ$ C. and 1 atm. The importance of chemical potential as a driving force for solid diffusion in minerals and rocks has already been elaborated upon by Bügge (1945).

The chemical potential gradient is, therefore, the force acting upon a solute atom in a system causing it to migrate, but in the case of self diffusion both the solute and the solvent atoms are chemically identical. There is, therefore, no chemical potential gradient in this case. Of course, no one has yet measured true self diffusion because there is no means of distinguishing the solute from the solvent. Very close approximations are obtained, however, by using stable or radioactive nuclides as tracers, even though this is not truly self diffusion as the nuclides of any element, of course, differ from the other nuclides of that element in mass.

The effect of impurities. The diffusion measurements made by chemists and metallurgists in the past have been performed almost entirely upon pure elements or compounds prepared in the laboratory. Now a mineral, is "a naturally occurring product" and, as a result, it is loaded with impurities. The significance of this is evident when one realizes the effect of impurities upon diffusion because, as we now know, the chemical potential of a substance can be affected significantly by slight differences in the concentration of another substance. The effect is generally an increase in the diffusion rate over the rate where no impurities are present.

Wagner & Hantelmann (1950) have shown the effect of adding given amounts of strontium chloride, as impurity, to potassium chloride. Measurements were made of the ionic conductivity of potassium chloride at given temperatures with varying amounts of strontium chloride in solid solution. The amount of strontium chloride present was always less than one per cent. The result was that the ionic conductivity of potassium chloride, which is proportional to ionic diffusion, increased considerably with slight additions of impurity. For example, at a temperature of 650° C, the ionic conductivity of potassium chloride,
containing 0.8 per cent strontium chloride, was found to be over 270 times the conductivity of pure potassium chloride. The explanation offered for the significant increase in diffusion is not only that the distortions introduced into the crystal lattice by the impurities create additional vacancies which, of course, allow more rapid diffusion, but also that even additional positive ion vacancies must exist for electrical neutrality as Sr\(^{++}\) is substituting for K\(^+\).

Minerals may contain several per cent of impure material which may easily vary from place to place in one crystal. Therefore, it is understandable why experimental diffusion measurements vary considerably from one specimen to another for a given mineral.

The presumed effect of impurities on diffusion rates is represented by figure 6. As we know, the slopes of the lines shown in this figure determine the energy of activation of the solute atoms in the system under investigation. It is suggested, therefore, that not only is the activation energy lowered (the slope is decreased) when impurities are added but the effect of impurities is decreased or overshadowed at higher temperatures when the expanded lattice would not then be as distorted.

**Effect of vapor pressure of mineralizer on diffusion rates.** Considering the abundance of information on diffusion coefficients determined by the metallurgical profession it is surprising to note the lack of information pertaining to the effect of pressure on diffusion rates. In fact even with the sparsity of simple diffusion experiments performed by the geological profession it is even more surprising to note that one of the
earliest reports on the effect of pressure on diffusion rates is reported in U.S. Geological Survey Prof. Paper 95-G (Van Orstrand & Dewey, 1915). In this very preliminary work, however, the metal (Au diffused into Pb) specimens were subjected to relatively low pressured applied by means of "oil" which had very little if any effect upon diffusion rates. In the conclusion of the paper, Van Orstrand does state, however, that the diffusion coefficients probably increase with pressure. On the other hand, Radavich & Smoluchowski (1944) noted a decrease in the diffusing rate of Cu in the Cu-Al system when subjected to elastic deformation by a stress of 7,000 kg/cm.².

Be that as it may, there is much somewhat indirect field evidence that diffusivity is increased, even appreciably, in minerals and rocks that exist in a medium of high vapor pressure — vapor pressure, for example, of mineralizers such as water or carbon dioxide or both. The indirect evidence is as follows:

1. The rate of crystal growth is controlled by the availability of the appropriate substances to a growing crystal surface. The rate of diffusion of the appropriate substances through a medium such as hydrothermal solutions or a pegmatitic solution lacking effective convection currents may, thus, influence the size of the resulting crystal. The majority of the crystals growing in viscous solutions, such as silica-rich hypabyssal and extrusive magmas, are relatively small. In contrast, the largest crystals generally occur in pegmatites from what is believed to have been an aqueous-rich (non-viscous) solution.

2. Determination of the orthoclase-albite binary phase diagram was accomplished (Bowen & Tuttle, 1950) by subjecting the appropriate mixtures to high water-vapor pressures in order to increase the rate of crystal growth. At one atmosphere, glass formed upon even slow cooling of the melt; with increased water vapor pressures, only cryptoperthites formed that could not be identified microscopically but had to be identified by x-ray techniques. This study is a striking example of the significant increase in the mobility or diffusion and resulting more rapid crystal growth of solute substances under increased vapor pressure of water.

3. Figure 7 is a photograph of a typical hand specimen from the Bingham porphyry copper stock, Utah. Hydrothermal alteration of feldspar crystals in this specimen has occurred presumably by diffusion of hydrothermal solutions (H₂O and CO₂ for the most part) into and through solid feldspar crystals to form various alteration minerals of clay and sericite. The distance of solid diffusion needed for this alteration is certainly not the diameter (several thousand feet) nor even the radius of the stock but instead, with few exceptions, is only a few
centimeters at the most. Hydrothermal solutions moved with relative ease through the myriad of fractures existing in the shattered portion of the Bingham stock. Note that the hand specimen itself (figure 7) exhibits without exception only vugs and planar surfaces or fracture planes along which the specimen broke when struck with a geologic hammer. Portions of some of these fractures are veinlets that are more than 1 cm. wide. Others are made evident only by thin lines on the planar surfaces of the specimen. The higher concentration of quartz and clay minerals along these fractures aids in accentuating the lines. Even so, disseminated sulfide specks and sericitized feldspar crystals do exist within the specimen, not along evident fractures, but near fractures from which diffusion transported the material along grain boundaries and ultimately into the crystals.

4. Finally, in order to obtain more direct evidence of the influence of vapor pressure on diffusion, initial laboratory diffusion experiments have been performed in the Laboratory of Economic Geology at Yale University wherein Yule marble specimens were subjected to water vapour pressures of about 300 bars. Small concentrations of NaCl containing tagged Na$^{22}$ atoms were dissolved in the water. It was, thus, possible to determine the diffusion coefficient of Na$^{22}$ in Yule marble at
given temperatures and known vapour pressures of water for comparison with similar experiments performed on Iceland spar, in order to determine the influence of crystal boundaries on diffusion rates, and of course the influence of variable vapour pressures. Initial results indicate diffusion rates near \(10^{-7} \text{ cm}^2/\text{sec.}\) for Na\(^{22}\) in Yule marble at 400° C. and \(~300\) bars vapour pressure. This is an increase in the diffusion coefficient of several powers of ten over the same experiment at the same temperature and at 1 atm. Further quantitative experimental work of this sort would be of prime interest and significance.

**Conclusions**

The migration or movement of atoms or ions in a solid substance is a fact. The rate of this process of solid diffusion can be measured experimentally and the results treated quantitatively by a rational mathematical approach. Diffusion appears to be of prime aid in the mechanisms by which various geological and mineralogical processes occur; *viz.*, hydrothermal alteration, replacement, crystal growth, and other even more controversial processes. The distances over which solid diffusion can be effective in these processes is relatively short, rarely more than several centimeters which is easily attainable by acceptable diffusion rates. Even so, transport of substances by "trunk lines" over considerably greater distances may be explained by relatively rapid movement through rock openings, along fracture zones, around mineral grains, and finally into crystals through crystal flaws and breaks. Solid diffusion transport through the remaining few centimeters is then effected with relative ease, resulting, thereby, in the transport and removal of a relatively large mass exchange of material.

As diffusion is a rate process, more knowledge about temperature conditions during diffusion and the thermodynamic properties of participating materials may enable one to determine the length of geological time needed during which diffusion dependent processes occurred.

**References**


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