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THEORETICAL STUDY OF THE DIFFUSION CONSTANT FOR
SELF-DIFFUSION IN METALS

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SUMMARY

An expression for the diffusion constant for self-diffusion in metals is derived, based on the assumption that self-diffusion occurs by the vacancy mechanism. The factors determining A in the expression $D = Ae^{-Q/RT}$, where D is the diffusion constant, Q is the energy of activation, R is the gas constant, and T is the temperature, are found to be the characteristic frequency of vibration of the atoms, the crystal structure, the lattice constant, the heat of fusion, the temperature, and the activation energy for an atomic jump. A comparison of the calculated values of A with the limited experimental data available shows that the calculated values are of the correct order of magnitude.

INTRODUCTION

Phenomena such as age-hardening, annealing, and order-disorder transformation depend on the ability of atoms to migrate through an atomic lattice. It is therefore of great importance to understand the factors that determine the rate at which such migration occurs. One method of determining the movements of atoms within a lattice is to study the rate at which metals diffuse into each other under controlled conditions. A special case of diffusion in metals is the case of self-diffusion.

The amount of material diffusing across a surface because of a difference in concentrations of a material is proportional to the concentration gradient at the surface, to the area of the surface, and to the time during which the process continues. The proportionalities can be converted to equalities by the introduction of a factor called the diffusion constant, which has the dimensions area per time. This diffusion constant D is not constant for a given material but depends on the temperature; the relation is given (reference 1) by

$$D = Ae^{-Q/RT} \quad (1)$$

where the coefficient A and the energy of activation Q are practically constant for large temperature intervals; R is the gas constant and T is the temperature in degrees Kelvin. In order to have a better understanding of the diffusion process, it is desirable to know the properties of the metals that determine the diffusion constant and consequently the rate of diffusion.

A number of generally known expressions for the diffusion constants for metals in the solid state exist (reference 2, p. 305). The Dushman-Langmuir expression (table I), which was derived by analogy with an earlier expression for the reaction-velocity constant (reference 2, p. 298), indicates that A depends on the lattice constant and on the energy of activation Q ; Bradley's expression, which was derived on the basis of kinetic theory and on the assumption that the distribution of energies among the atoms was a Maxwell-Boltzmann distribution, indicates that A depends on the lattice constant, on the frequency of vibration of the atoms, on Q , and on the temperature; Cichocki's expression, which was derived on a probability basis and on the assumption that the atoms become ionized in the process of making a jump, indicates that A depends on the melting temperature and on atomic weight and volume. More recently, on the basis of rate-process theory, Eyring has developed an expression for D (reference 3, p. 538) in which A depends on atomic volume, temperature, and the Debye characteristic temperature. The preceding expressions were derived for the general case of diffusion and as shown in table I only the Dushman-Langmuir formula yields results of the correct order of magnitude for the special case of self-diffusion. The Dushman-Langmuir formula is, however, semiempirical, having been derived without the use of any assumptions as to the mechanism by which diffusion occurs and consequently it does not explicitly show the properties of the metals that most directly affect the diffusion constant.

Although many expressions exist for the diffusion constant, the mechanism of diffusion suggested by Frenkel (reference 2, p. 293) is generally accepted. According to the Frenkel theory, diffusion is the result of atoms jumping into vacant sites, or holes, in the lattice. A vacancy is generated in the lattice when an atom jumps from its normal site to an interstitial position, or when an atom escapes from its normal site at some internal surface, without occupying an interstitial position. Schottky has shown (reference 4, p. 69)

that the first process is more likely in a lattice consisting of atoms whose radii differ greatly from each other; whereas the second process is more likely if the atoms have approximately equal radii.

In a theoretical study made at the NACA Lewis laboratory, only self-diffusion of metals was considered.

SYMBOLS

The following symbols are used in this report:

A	constant
D	diffusion constant
d	average length of atomic jumps
E_f	heat of fusion
E_g	heat of sublimation at 0° K
E_0	average energy of vacancy formation
E_t	average thermal energy
E_1	average energy required to make one jump
F	fraction of atoms having energy equal to or greater than E_1
J_a	number of jumps per second for atom
J_{max}	maximum possible number of jumps per second for vacancy
J_0	number of jumps per second for vacancy
m	mass of atom
N	number of atoms per unit "cell"
N_a	number of atoms per unit volume
N_0	number of vacancies per unit volume
Q	energy of activation

R	gas constant
T	temperature
t	time
t_0	time required for vacancy to make one jump
V	velocity of jumping atom
v	instantaneous velocity of vibrating atom
v_{max}	maximum velocity of vibrating atom
W	number of nearest neighbors in lattice
x	displacement of vibrating atom
x_0	amplitude of vibrating atom
ν	frequency of vibration

ANALYSIS

The formation of a vacancy at an internal surface has one of two possible results. The vacancy may either be reoccupied by the atom that has just vacated it, in which case no diffusion occurs, or it may be occupied by a different neighboring atom, which leads to diffusion. It is shown in reference 3 (p. 519) that if J_a is the average rate at which each atom jumps, the diffusion constant D is given by

$$D = J_a d^2 \quad (2)$$

where d is the average length of the jumps, the jumps having only one degree of freedom. For three degrees of freedom, the equation becomes

$$D = \frac{J_a d^2}{3} \quad (3)$$

It will now be shown that J_a can be expressed in terms of the number of vacancies per unit volume in the lattice N_0 and the average number of jumps per second made by each vacancy J_0 .

Only atoms adjacent to a vacancy can make jumps. Over a long period, however, each atom will have had the same number of opportunities for jumping, so that the average number of jumps per second will be the same for all atoms. If a unit volume of the metal under consideration is divided into N_0 equal volumes, or "cells," each cell will, on the average, contain one vacancy. If N is the number of atoms in a cell, the average number of jumps for any atom in a given cell will be $1/N$ times the total number of jumps. Therefore the number of jumps per second for an atom is $1/N$ times the number of jumps per second for a vacancy. In symbol form,

$$J_a = J_0/N \quad (4)$$

The number of atoms N in a cell is given by

$$N = N_a/N_0 \quad (5)$$

where N_a is the number of atoms per unit volume. Substitution of equation (5) into equation (4) and then of equation (4) into equation (3) yields

$$D = \frac{J_0 N_0}{3N_a} d^2 \quad (6)$$

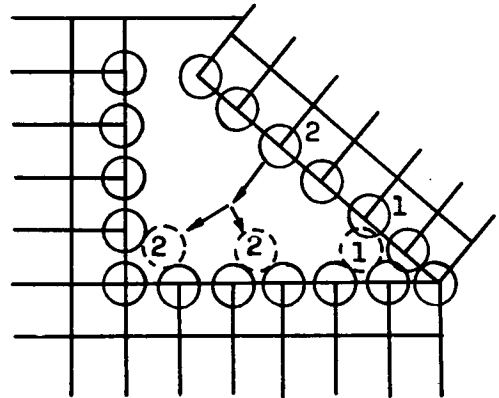
The value of N_0 depends on the number of atoms having sufficient energy E_0 to escape from their normal sites. For a lattice containing vacancies but no interstitial atoms, the total number of vacancies per unit volume, when the lattice is in equilibrium, is given (reference 4, pp. 63 and 65) by

$$N_0 = N_a e^{-E_g/2RT} \quad (7)$$

where E_g is the energy of sublimation at absolute zero. Because it is desirable to know N_0 as a function of E_0 rather than as a function of E_g , it is necessary to find a relation between E_0 and E_g .

The following diagram is a schematic representation of an internal surface. A vacancy is formed whenever one of the atoms acquires sufficient energy to jump from its original position to some other equilibrium position. Some atoms, such as atom 1, are so located that they can reach a new equilibrium position without appreciably changing their distance from their nearest neighbors. The

energy required for such motion is equal to the heat of fusion. An atom such as atom 2, however, must jump a large distance in order to break the bonds of its nearest neighbors. It is assumed that the distance atom 2 has to jump is large enough that the energy necessary for the jump is equal to the sublimation energy. Although a vacancy is more likely to form at a place such as the site occupied by atom 1 because less energy is required, the vacancy formed at such a point will be partly blocked by the atom that has vacated the site, thus seriously interfering with further diffusion. As a first approximation, it will therefore be assumed that the average energy of vacancy formation E_0 is the arithmetic average of the minimum and maximum energies of vacancy formation. The sublimation energy at high temperatures is approximately equal to the sublimation energy at absolute zero (reference 5), and therefore, E_g may be used for the maximum energy of vacancy formation. That is,



$$E_0 = \frac{1}{2} (E_g + E_f)$$

$$E_g = 2E_0 - E_f \quad (8)$$

Substitution of equation (8) into equation (7) yields

$$N_0 = N_a e^{E_f/2RT} e^{-E_0/RT} \quad (9)$$

In the determination of J_0 , the assumption is made that, on the average, an atom (providing it has sufficient energy) begins its jump as soon as a neighboring atom has exceeded its normal amplitude in the course of making a jump. Because the atoms are executing simple harmonic motion (in three dimensions), the equation of motion in the x -direction is

$$x = x_0 \sin 2\pi\nu t$$

where x is the displacement, x_0 the amplitude, ν the frequency, and t the time. Differentiation of the preceding equation yields

$$\frac{dx}{dt} = v = 2\pi\nu x_0 \cos 2\pi\nu t$$

When $t = 0$, $v = v_{\max}$; therefore

$$x_0 = \frac{v_{\max}}{2\pi\nu} \quad (10)$$

When a Maxwell-Boltzmann distribution of energies is assumed, the average energy for each degree of freedom is RT (reference 6). The total thermal energy E_t is $3RT$ and therefore the average energy for each degree of freedom is $1/3 E_t$. The maximum velocity v_{\max} can then be determined as follows:

$$\frac{1}{2} m v_{\max}^2 = 1/3 E_t$$

or

$$v_{\max} = \sqrt{2E_t/3m} \quad (11)$$

Substitution of equation (11) into equation (10) yields

$$x_0 = \frac{\sqrt{2E_t/3m}}{2\pi\nu}$$

Let E_1 be the energy necessary to make a jump. Then the velocity V of the atom while it has the energy E_1 can be determined from the equation

$$\frac{1}{2} m V^2 = E_1$$

or

$$V = \sqrt{2E_1/m}$$

If it is assumed that the velocity of the atom remains constant while the atom is moving through the distance x_0 (x_0 is only a small fraction - about $1/25$ - of the entire jump), the time t_0 required to traverse the distance x_0 is

$$t_0 = x_0/v$$

$$t_0 = \frac{\sqrt{2E_t/3m}}{2\pi v}$$

$$t_0 = \frac{\sqrt{E_t/3E_1}}{2\pi v}$$

If t_0 is considered to be the time required for the vacancy to make one jump, the maximum number of jumps per second J_{\max} that a given vacancy can make is

$$J_{\max} = \frac{1}{t_0}$$

$$J_{\max} = \frac{2\pi v}{\sqrt{E_t/3E_1}} \quad (12)$$

But a jump occurs only when one of the atoms near a vacancy has an amount of energy equal to or greater than E_1 . For a Maxwell-Boltzmann distribution of energies, the fraction of the atoms having energy equal to or greater than E_1 is

$$F = e^{-E_1/RT} \quad (13)$$

Because at all times $e^{-E_1/RT}$ of the atoms have sufficient energy to make a jump, it is also true that each atom has sufficient energy $e^{-E_1/RT}$ of the time. If each vacancy had one nearest neighbor, the number of jumps per second would be given by FJ_{\max} . But if each vacancy has, for instance, W nearest neighbors, the number of jumps per second J_0 is given very nearly by

$$J_0 = WFJ_{\max} \quad (14)$$

When the values of F and J_{\max} as given by equations (13) and (12), respectively, are substituted into equation (14), there results

$$J_0 = 2\pi v W \sqrt{3E_1/E_t} e^{-E_1/RT} \quad (15)$$

Substitution of equations (15) and (9) into equation (6) yields

$$D = \frac{2\pi\Omega}{3} W \sqrt{3E_1/E_t} d^2 e^{E_f/2RT} e^{-(E_0 + E_1)/RT} \quad (16)$$

Consequently, from a comparison of equations (1) and (16)

$$A = \frac{2\pi\Omega}{3} W \sqrt{3E_1/E_t} d^2 e^{E_f/2RT} \quad (17)$$

COMPARISON OF CALCULATED AND EXPERIMENTAL DATA

All the data available for metals with symmetric crystal structure are for face-centered cubic lattices. The number of nearest neighbors is the same for all materials of this type and is equal to 12. When all the constants of equation (17) are combined, A becomes

$$A = 43.6\Omega d^2 \sqrt{E_1/E_t} e^{E_f/2RT} \quad (18)$$

The average length of the jumps is assumed to be equal to the lattice constant. Equation (18) can be applied to determine the value of A if $\sqrt{E_1/E_t}$ can be approximated, inasmuch as all the other parameters are known.

On the basis of existing data (reference 2, p. 275) the maximum value of Q is about 60,000 calories per mole, that is,

$$E_0 + E_1 \cong 60,000$$

Theoretically the smallest value that E_0 can have is the heat of fusion E_f , which for copper, gold, and silver is approximately 3000 calories per mole. The smallest value for E_0 yields the largest theoretically possible value for E_1 . That is, if $E_0 = E_f$

$$E_f + E_1 \cong 60,000$$

$$E_1 \cong 60,000 - 3000 \cong 57,000$$

$$\sqrt{E_1/E_t} \cong \sqrt{57,000/E_t}$$

and

$$E_t = 3RT \cong 6T$$

The center of the temperature range in which experiments are conducted is approximately 1000° K (for copper, gold, and silver). At this temperature, the maximum theoretically possible value for

$$\sqrt{E_1/E_t} \cong \sqrt{57,000/6000} = 3.08.$$

It is more reasonable to assume that

$$E_0 \cong E_1$$

For this case,

$$2E_1 \cong 60,000$$

$$E_1 \cong 30,000$$

and

$$\sqrt{E_1/E_t} = \sqrt{30,000/6000} \cong 2.24$$

For lead, the center of the temperature range is about 500° K and Q is about 28,000 calories per mole. Therefore,

$$E_1 \cong 14,000$$

and

$$\sqrt{E_1/E_t} \cong \sqrt{14,000/3000} \cong 2.16$$

From the preceding considerations it can be seen that $\sqrt{E_1/E_t}$ is to a large extent independent of material as well as of temperature, having a value approximately between 2 and 3. If $\sqrt{E_1/E_t}$ is set equal to 2.5, equation (18) becomes

$$A = 109 v d^2 e^{E_f/2RT} \quad (19)$$

Although equation (19) shows that A is a function of the temperature, the calculated value of A is only about one and one-half times as great at 750° K as it is at 1250° K. Inasmuch as the experimental values of A , which are independent of temperature, show a greater variation, A will only be evaluated at 1000° K for gold, copper, and silver, and at 500° K for lead.

The value of A can be calculated for the metals for which self-diffusion data exist by using the data in table II. The experimental and calculated values of A are contained in table I.

Another comparison can be made with previous calculations. On the basis of the random-walk theory, Weinbaum (reference 7) has calculated that the average number of jumps per second J_a for the atoms of a silver lattice at a temperature of 1149° K (876° C) is 6.3×10^6 . Equations (4) and (5) can also be used to calculate the number of jumps per second under the aforementioned conditions.

$$J_a = \frac{J_o N_o}{N_a}$$

Substituting equations (15) and (9) for J_o and N_o , respectively, and combining constants yields

$$J_a = 324 \nu e^{E_f/2RT} e^{-(E_o + E_1)/RT}$$

For silver, $Q = 45,950$ calories per mole (reference 8). At 1149° K

$$J_a = 5.8 \times 10^6$$

SUMMARY OF ANALYSIS

An expression for the diffusion constant for self-diffusion has been derived and has been found to give results that are of the right order of magnitude. The coefficient A in the expression $D = Ae^{-Q/RT}$, where D is the diffusion constant, Q is the energy of activation, R is the gas constant, and T is the temperature, is determined by the characteristic frequency of vibrations of the atoms, the crystal structure, the lattice constant, the heat of fusion, the temperature, and the activation energy for an atomic jump. More data are needed, however, before definite conclusions can be drawn regarding the applicability of the expression.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, February 2, 1949.

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TABLE I - COMPARISON OF CALCULATED AND EXPERIMENTAL
VALUES OF A FOR EQUATION
 $D = Ae^{-Q/RT}$

Metal	Experimental values of A (cm ² /sec)		Calculated values of A (cm ² /sec)					
		Reference	(a)	(b)	(c)	(d)	(e)	(f)
Lead	5.1 6.66	2, p. 274 9	0.88	0.71	2.0×10^{-2}	3.7×10^{-3}	4.2×10^{-3}	4.5×10^5
Silver	1.0 .895	10 8	1.6	0.74 .80	2.6×10^{-2} 2.8	6.4×10^{-3}	2.1×10^{-3}	7.8×10^5
Copper	11 47	2, p. 274 9	2.0	0.78 .84	4.2×10^{-2} 4.4	7.3×10^{-3}	2.3×10^{-3}	
Gold	2 126 410	9 2, p. 274 9	1.5	0.88 .88 1.1	2.6×10^{-2} 2.6 3.2	5.3×10^{-3}	1.7×10^{-3}	1.2×10^6



^a $A = \frac{2m\phi W}{3} \sqrt{3E_1/E_t} d^2 e^{E_f/2RT}$ (equation (17)).

^b $A = \frac{Q}{Nh} d^2$ (Dushman-Langmuir), where N is Avogadro's number and h is Planck's constant.

^c $A = \frac{1}{6} \frac{Q}{RT} v d^2$ (Bradley).

^d $A = \frac{8v}{3\pi} d^2$ (van Liempt).

^e $A = \left(\frac{V}{N}\right)^{2/3} \frac{kT}{h} (1 - e^{-3\theta/4T})$ (Eyring), where V is the gram atomic volume, k is the Boltzmann constant, and θ is the Debye characteristic temperature.

^f $A = 2.43 \times 10^4 \frac{M}{V} \sqrt{\frac{T_s}{M}}$ (Cichocki), where M, V, and T_s are atomic weight, atomic volume, and melting temperature, respectively. For values of M, V, and T_s , see reference 11.

TABLE II - PARAMETERS FOR EQUATION (19)

Metal	E_f (cal/mole) (a)	ν (vibrations/sec)	d (cm) (c)
Copper	3110	^b 6.6×10^{12}	3.61×10^{-8}
Gold	3030	^d 3.8	4.07
Silver	2700	^b 4.5	4.08
Lead	1220	^b 1.8	4.94

^aData from reference 5, p. 259.

^bData from reference 12.

^cData from reference 13.

^dComputed from $\nu = k\theta/h$ where k is Boltzmann constant, h is Planck's constant, and θ , the Debye temperature for gold, is 180 (reference 5, p. 237).

