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Diffusion Coefficient of C in α-Iron*

C. A. WERT
Institute for the Study of Metals, University of Chicago, Chicago, Illinois

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An equation of the form $D=D_0e^{-\Delta H/RT}$ is developed for interstitial diffusion in cubic lattices. This development uses a classical statistical mechanical treatment. Measurements of D for C in α-iron were made from $-35°$ to 200°C. Combined with earlier data they extend the knowledge of D in this system from $D=10^{-20}$ to $D=10^{-6}$ cm²/sec. The values of D_0 and ΔH obtained by fitting the above equation to the experimental points give $D_0=0.02$ cm²/sec. and $\Delta H=20{,}100$ cal./mole.

I. INTRODUCTION

NUMEROUS attempts have been made in the past to find an equation which describes adequately the process of diffusion in solids. These investigations have in general resulted in equations expressing the diffusion coefficient, D, in terms of such parameters as lattice geometry, temperature, and energy.[1] Experimental measurements which would test these theories have not been highly successful. There are two reasons for this: (1) some of the theories have resulted in relations containing parameters not easily measurable, and (2) the value of D has not been measured accurately enough, nor over a sufficient range, to permit adequate testing of the different expressions. The present investigation was a further attempt to solve this problem in a carefully selected alloy system using experimental techniques only recently developed. The investigation had two formal purposes: (1) to find an expression for D for diffusion of interstitial solute atoms in terms of measurable quantities, and (2) to test this expression by making measurements covering as wide as range in D as possible.

In Section II an expression for D will be developed; in Section III the experimental techniques used in the various temperature ranges will be discussed; and in Section IV the results of the experimental work will be presented.

II. ANALYSIS

Diffusion of the solute atoms in an interstitial solid solution is more easily analyzed than is diffusion in substitutional alloys. For an interstitial atom the diffusion mechanism is simply the jumping of the diffusing atom from one interstitial site to another. For a substitutional atom the mechanism has not yet been established by experiment. The following discussion is a classical, statistical mechanical, derivation of an equation for D which applies to the interstitial diffusion of dilute solid solutions. It is a simple problem in random walk to show that for interstitial diffusion in a cubic lattice the diffusion coefficient D is given by the expression[2]

$$D=\alpha(a^2/\tau), \tag{1}$$

where α is a constant depending on crystal geometry, a is the lattice parameter, and τ is the mean-time-of-stay of an atom at a given lattice site. The coefficient α is easily computed; it is found to be 1/12 for f.c.c. and 1/24 for b.c.c. lattices. The lattice parameter is, of course, well known for most common materials. To determine D it is only necessary to measure τ directly or to evaluate it from other known measurements. It is the purpose of the remainder of this section to find an expression for τ.

There have been developed a number of expressions for τ.[1] One group of these expressions has depended on a general investigation of the statistical theory of reaction rates by Eyring.[3] Though this rate theory is immediately applicable to the problem of diffusion, it is the opinion of the present author that it has not been applied in its most useful form. In the discussion which follows there will be presented a short derivation of τ which parallels the Eyring investigation to a certain point but which finally leads to a similar expression which is capable of much more direct physical interpretation. Though Eyring's development followed a quantum-mechanical treatment, it is sufficient to consider this interstitial diffusion problem from the point of view of classical statistics.

It is clear that in passing from one lattice site to another, the solute atom must have sufficient energy to pass over a potential barrier; the rate of jumping is then determined by the fraction of the time that an atom has this requisite energy. This is strictly true, of course, only if the interstitial site to which the atom would like to move is unoccupied; it is assumed that this is the case for the dilute solid solution considered here. In the discussion to follow, I will use the following nomenclature. x is the coordinate along a line connecting the interstitial sites. The coordinate of one interstitial site is $x_0=0$ and that of an adjacent site is $x=x_1$.

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[1] For a recent summary of this work see B. Chalmers, *Progress in Metal Physics* (Interscience Publishers, Inc., New York, 1949), Chapter 7.

[2] See for example C. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).

[3] H. Eyring, J. Chem. Phys. **3**, 107 (1935). Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

x' is the position of the top of the potential barrier over which the particle must pass to go from x_0 to x_1. Let N be the number of particles in the site about x_0 and n the linear density of particles at x'. If $\bar{v}$ is the average velocity of all particles at x' crossing the barrier from the site at x_0 to x_1, then the rate at which particles pass the position x' is given by $n\bar{v}/N$. This flux of particles is proportional to the reciprocal of the mean-time-of-stay, τ, of the particles in the potential hole about x_0. It is assumed that the transmission coefficient of the barrier is unity. This assumption will be shown in Section IV to be consistent with the analysis of the experimental data. Thus

$$1/\tau = n'n\bar{v}/N, \tag{2}$$

where n' is the number of equivalent paths of diffusion from a given lattice site.

One must now evaluate the right member of this equation. To do this properly, one must first consider the number of coordinates of motion involved. To be sure, the "path of reaction" lies along x, but the diffusing atom may also oscillate in the y and z directions. In addition it is evident that some motion of the solvent atoms themselves may be involved. It is not clear how many of these atoms may be involved nor in detail how the atoms may move, but their motion may be formally introduced into the expression for $1/\tau$. The analysis of the data in Section IV will indicate that this is consistent with the experimental facts. In the light of these considerations Eq. (2) becomes

$$\frac{1}{\tau} = n' \frac{\int_{\infty}^{\infty} \cdots \int \exp[-\phi(x', y, z, q_i)/kT] dydz \prod_i dq_i}{\int_{-\infty}^{\infty} \cdots \int \exp[-\phi(x, y, z, q_i)/kT] dxdydz \prod_i dq_i} \cdot \frac{\int_0^{\infty} \frac{P_x}{M} \exp[-P_x^2/2MkT] dp_x}{\int_{-\infty}^{\infty} \frac{P_x}{M} \exp[-P_x^2/2MkT] dp_x}. \tag{3}$$

In this expression the first fraction represents the ratio n/M, the second, $\bar{v}$. The function $\phi(x', y, z, q_i)$ is the potential energy of the system (diffusing atom plus adjacent solute atoms) when the diffusing atom is at the position x'. The function $\phi(x, y, z, q_i)$ is the general potential energy of the system. The momentum of the diffusing atom is p_x, its mass, M. The q_i represent the coordinates of the unknown number of solute atoms which participate in the jumping. Since ϕ is unknown away from x_0, this expression cannot be evaluated in general. However, if the height of the barrier is large compared with kT, not much error is introduced by replacing in the denominator of Eq. (3) the function ϕ by $[\phi(x_0, y, z, q_i) + \frac{1}{2}Kx^2]$, where K is the force constant for a small region about $x_0 = 0$. With this approximation Eq. (3) becomes

$$\frac{1}{\tau} = n' \frac{\int_{-\infty}^{\infty} \cdots \int \exp[-\phi(x', y, z, q_i)/kT] dydz \prod_i dq_i}{\int_{-\infty}^{\infty} \cdots \int \exp[-\phi(x_v, y, z, q_i)/kT] dydz \prod_i dq_i} \cdot \frac{\int_0^{\infty} \frac{P_x}{M} \exp[-P_x^2/2MkT] dp_x}{\int\int_{\infty}^{\infty} \frac{P_x}{M} \exp\left[-P_x^2/2MkT - \frac{kx^2}{2kT}\right] dp_x dx}. \tag{4}$$

The second factor can be evaluated to yield $(1/2\pi)(K/M)^{\frac{1}{2}}$; this is just the frequency, ν, of small oscillations about x_0. The first fraction represents the ratio of two partition functions, the numerator that for the system with the particle moving in the yz plane at x', the denominator that for the system with the particle moving in the yz plane at x_0. Thus

$$1/\tau = n'\nu P'/P_0. \tag{5}$$

For comparison one would write a corresponding equation from the work of Eyring[3] and others

$$1/\tau = n'kTP'/hP_0^*. \tag{6}$$

Here kT/h represents the quantum-mechanical "frequency factor" and P' the same function as in Eq. (5). P_0^* on the other hand is different from P_0 since P_0^* still contains integration over the coordinate x; such integration has been carried out explicitly in Eq. (5). We will see at once that it is on precisely this point that the present work deviates from that of Eyring.

In terms of thermodynamical functions Eq. (5) can be written

$$1/\tau = n'\nu \exp[-\Delta G/RT]. \tag{7}$$

Here ΔG is the work done when a mole of solute atoms is moved isothermally from x_0 to x' at constant pressure. Since

$$\Delta G = \Delta H - T\Delta S,$$

Eq. (7) finally becomes

$$1/\tau = n'\nu \exp[\Delta S/R] \exp[-\Delta H/RT]. \tag{8}$$

Equation (1) can now be written

$$D = \alpha a^2 n'\nu \exp[\Delta S/R] \exp[-\Delta H/RT]. \tag{9}$$

ΔS and ΔH are termed the entropy and entalpy of activation; since there is at present no way to calculate these quantities, they must be determined by experiment. Such a determination is made in Section IV.

Eyring's analog to Eq. (7) is[3]

$$1/\tau = n'(kT/h) \exp[-\Delta F^*/RT], \tag{10}$$

where ΔF^* is again termed the "free energy of activation." From this expression it follows that

$$1/\tau = n'(kT/h)\exp[\Delta S^*/R]\exp[-\Delta H^*/RT], \quad (11)$$

where ΔS^* and ΔH^* are corresponding entropy and heat of activation. Since Eqs. (8) and (10) have been derived using the same general method and with the same initial assumptions, they ought to be equivalent and formally they are. Any apparent difference must be one of interpretation; this difference may be expressed in this way. We have seen in Eq. (7) that ΔG represents the work necessary to move isothermally from x_0 to x' one mole of solute atoms which are oscillating in the yz plane—both the initial and final states represents the same number of degrees of freedom for the solute atom. In Eq. (10), ΔF^* represents the work necessary to move isothermally from x_0 to x' a mole of atoms which have one more degree of freedom at x_0 than they do at x'—namely, the coordinate x. This is a direct result of the fact that in Eq. (6) P_0^* contains one more degree of freedom than P'. It seems to the present writer that ΔG as defined above thus has a much more reasonable physical interpretation than does ΔF^*. Hence, Eq. (7) is preferred at least in this simple case to Eq. (10).[4]

III. METHOD OF EXPERIMENT

The experimental values of D to be reported in Section IV are for the diffusion of C in α-iron. Those values of D determined in this laboratory were made by direct use of Eq. (1). Since α and a are well known for the b.c.c. α-iron, the only further measurement needed was the value of τ as a function of temperature. This was found by measuring, at selected temperatures, the relaxation time, τ_r, which will be shown to be related simply to τ. The relaxation time can be described in the following way: At equilibrium under no stress the atoms of carbon arrange themselves in equal numbers among the three types of lattice positions, the x, y, z sites. This can be expressed by writing $N_x^0 = N_y^0 = N_z^0 = N/3$. Let this equilibrium be disturbed by the transfer of an equal number of atoms from the y and z positions to the x position. (A carbon atom which migrates to, say, an x position has an equal chance of coming from a y or a z position; it cannot come directly from another x position.) The state of affairs is then expressed by the relations

$$N_x = N_x^0 + \Delta n',$$
$$N_y = N_z = \tfrac{1}{3}N - \tfrac{1}{2}\Delta n'.$$

The rate at which equilibrium is approached is given by the well-known exponential decay law

$$d(\Delta n)/dt = -\Delta n/\tau_r, \quad (12)$$

where Δn is the net number of atoms which must yet migrate for the equilibrium to be established, and τ_r is the relaxation time.

The relationship between τ and τ_r for a b.c.c. lattice is given by the equation

$$\tau = \tfrac{3}{2}\tau_r. \quad (13)$$

That this is true can be seen from the following argument. The probability for an atom which is at a given lattice site at time $t=0$ of remaining in that site is given by

$$P(t) = e^{-t/\tau}.$$

If N_x, N_y, and N_z be the number of atoms in positions x, y, and z then change in the number of atoms in, say, the x position in a time Δt short compared to τ is

$$\frac{dN_x}{dt}\Delta t = -\frac{N_x}{\tau}\Delta t + \frac{N_y}{2\tau}\Delta t + \frac{N_z}{2\tau}\Delta t. \quad (14)$$

Since $N_x + N_y + N_z = N$, Eq. (14) can be written as

$$dN_x/dt = -(N_x/\tau) + (N - N_x)/2\tau$$

which is equivalent to

$$d(N_x - \tfrac{1}{3}N)/dt = -3(N_x - \tfrac{1}{3}N)/2\tau.$$

In terms of quantities used in the preceding paragraph, this equation becomes

$$d\Delta n/dt = -3\Delta n/2\tau. \quad (15)$$

Equation (13) follows at once from a comparison of

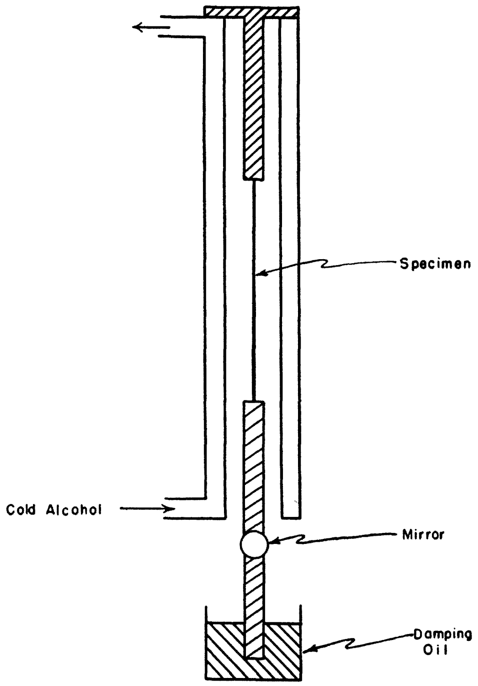

FIG. 1. Schematic diagram of apparatus used to measure elastic aftereffect.

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[4] It has been shown by Wert and Zener (reference 2) that by appropriate treatment of Eq. (6) one can arrive also at Eq. (7).

Eqs. (12) and (15). It follows from Eqs. (1) and (13) that D can be computed once τ_r is known.

The relaxation times at different temperatures were measured by different experimental methods; use of a given method depended upon the magnitude of τ_r at a given temperature. At temperatures in the neighborhood of 0°C and less, the elastic aftereffect was used. At somewhat higher temperatures τ_r was measured by the internal friction method; at temperatures of about 40°C a torsional pendulum was used at approximately 1 c.p.s.; at 90° and 125°C a magnetic drive method was used at 100 and 1000 c.p.s., respectively. At still higher temperatures, a precipitation method was used. A brief description of these various methods follows.

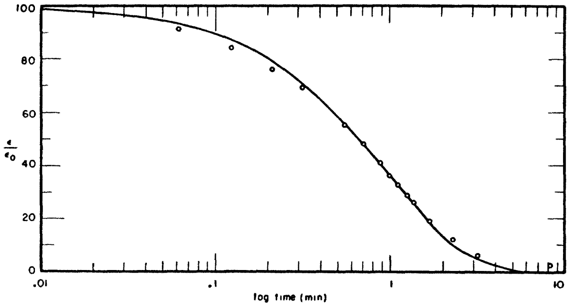

FIG. 2. Elastic aftereffect of C in α-iron at −10°C. $\epsilon=\epsilon_0 e^{-t/.98}$.

The elastic aftereffect has previously been employed to measure relaxation phenomena.[5] In the present case the experiment was performed in the following way:

The specimen (a wire of iron 0.03 in. in diameter and 1 foot long containing about 0.02 wt. percent C in solid solution) was mounted vertically inside a double-walled round chamber shown schematically in Fig. 1. Cold alcohol was circulated in the region between the concentric walls to cool the inside of the chamber. A light beam was focused on a scale three meters away by a mirror. With this arrangement the angular deflection of the mirror from an equilibrium position could be determined. The wire is held rigidly at the top by its supporting member. In making a measurement of τ_r the bottom support was first twisted through about 10° around its vertical axis and held there for some time. Then the bottom support was released. The angular deflection did not immediately become zero; approximately five percent of the previous strain (about 0.5°) still remained. This recoverable anelastic strain gradually reduced to zero; the measurement consisted in measuring this strain as a function of time.

A measurement at −10°C is shown in Fig. 2. Here the experimental points are fitted with the exponential form

$$\epsilon=\epsilon_0 \exp(-t/\tau_r) \tag{16}$$

where t is the time after release of the bottom supporting member. It is seen that the experimental points do not fit the exponential exactly; the reason for this is not known. However, an average can be determined to an accuracy of at least 15 percent, which is adequate for our purposes.

The internal friction measurements with the torsional pendulum[2] and with the magnetic drive apparatus[5,6] are adequately described. The observation consists in a measurement of the temperature at which the maximum occurs in the internal friction for a given frequency, ω. Then τ_r is determined from the relation $\tau_r=1/\omega$. For the torsional pendulum, the specimens were wires 0.03 in. in diameter and 1 foot long. For the magnetic-drive method the specimens were two light bars of iron. One of these was about 1 foot long and about 0.1 in. in diameter; this gave resonance in flexural oscillations at about 100 c.p.s. The other was about 6 in. long and about 0.15 in. in diameter; it was resonant at about 1000 c.p.s.

It was at first thought to be reasonable to carry the internal friction type of measurements to higher temperatures by going to higher frequencies. This was prevented by the occurrence of rapid precipitation into Fe_3C of the supersaturated solid solution of C; such a process made good data difficult to obtain. However, by making use of the phenomenon of precipitation itself, two additional points at higher temperatures were obtained. The method is explained in this way. Let a highly supersaturated solution of carbon in α-Fe be prepared. Precipitate this carbon at some temperature T_1 and measure the amount of precipitate as a function of time. Find the time t_1 at which say half of the carbon has precipitated. Redissolve the precipitate at high temperature, quench, and reprecipitate say 10 percent of the carbon at T_1. Let the time required for this be t_0. Complete the precipitation at some higher temperature T_2. Let the time required for 50 percent of the transformation be t_2. These times are shown schematically

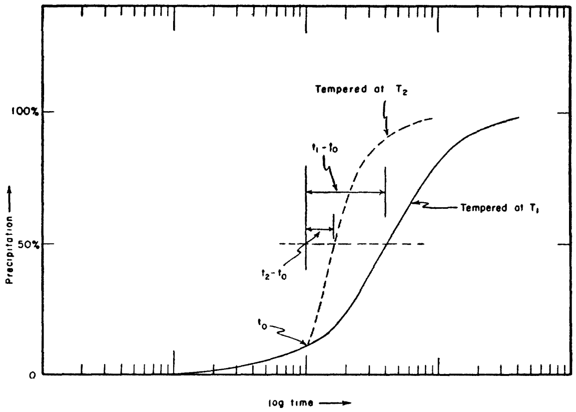

FIG. 3. Precipitation at temperatures T_1 and T_2 following nucleation at T_1.

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[5] C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, 1948).

[6] T. S. Kê, J. Metals (to be published).

in Fig. 3. It can be shown readily from earlier results from this laboratory[7] that under the conditions of the experiment the diffusion coefficients D_1 and D_2 at T_1 and T_2 are related by the equation

$$D_2 = D_1(t_1 - t_0)/(t_2 - t_0).$$

If D_1 is known, D_2 can be computed.

IV. EXPERIMENTAL RESULTS

The results of all the measurements are shown in Fig. 4 in which $\log D$ is plotted as a function of $1/T$. Four measurements were made by the elastic aftereffect technique, five with the torsional pendulum, two by the higher frequency internal friction method, and two more using the precipitation method. These last two points were made in two stages. One step was from 125° (where D had previously been measured) to 150°C; the next step going from 150° to 200°C. It seemed unwise to go any further than this since the measurements are not independent and errors are cumulative. These last two points are for this reason probably the least reliable.

The very high temperature data are from work reported by Stanley,[8] and were made by chemical analysis following bulk diffusion of C from a high (0.02 wt. percent) to a low carbon alloy. The remaining three points are computed from some carefully done work of Richter who in 1938 reported an aftereffect in carbonyl iron.[9] Though he did not know the cause of the effect which he observed, it appears from the agreement of his results with the present data that he, too, was measuring the relaxation effect of C in his material.

The solid line in Fig. 4 was drawn according to the equation

$$D = D_0 e^{-\Delta H/RT} \tag{17}$$

where D_0, according to Eq. (9), is

$$D = \alpha a^2 \nu n' e^{\Delta S/R}. \tag{18}$$

The parameters D_0 and ΔH in Eq. (17) were adjusted to give the best fit to the data (excluding that of Richter); these values are $D_0 = 0.02$ cm²/sec. and $\Delta H = 20{,}100$ cal./mole. In Fig. 4 it is seen that the fit of Eq. (17) to the data is good. Using Eq. (18) it is possible to compute ΔS; such a computation gives $\Delta S \approx 5$ cal./mole °C. This value of ΔS is in good agreement with earlier work of Wert and Zener[2] concerning the theoretical range of ΔS. According to them ΔS may have the range zero to 5 cal./mole °C. Since the value of ΔS computed above, namely about 5 cal./mole °C, is near the top of the predicted range, a large part of the energy of activation must go into lattice strain energy. In passing it might be well to note that this calculation indicates that the transmission coefficient mentioned earlier is of the order unity. If it were considerably less than 1, the factor $e^{\Delta S/R}$ in Eq. (18) would have to be larger so that D_0 could keep its experimentally determined value. A very large increase in ΔS would be difficult to explain; hence, the conclusion must be that for the present case, the transmission coefficient is of order 1.

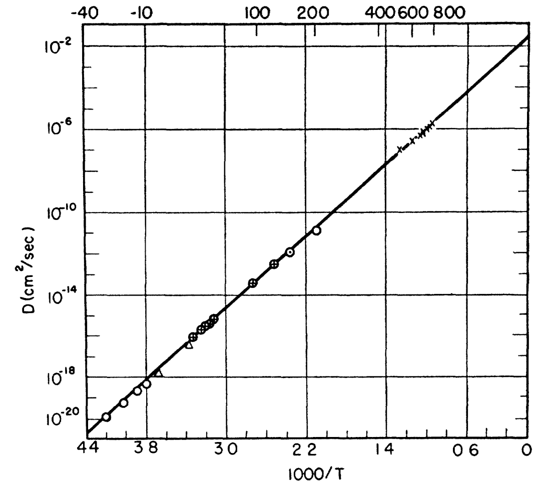

FIG. 4. Diffusion coefficient of C in α-iron as a function of $1/T$. The experimental data are identified in the following way: Elastic aftereffect—○; internal friction—⊕; precipitation measurements—⊙; elastic aftereffect (Richter)—△; bulk diffusion measurements (Stanley)—×. The straight line is drawn according to the relation $D = D_0 \exp(-\Delta H/RT)$.

Because of the thermodynamic properties of ΔG, ΔS, and ΔH, it can be shown that

$$d(\ln D)/d(1/T) = \Delta H/R.$$

This means that at any temperature the slope of the curve in Fig. 4 gives the value of ΔH at that temperature. This is true regardless of how ΔH and ΔS might vary with temperature. That the experimental points in Fig. 4 can be fitted with a straight line means that over this temperature range ΔH is constant. This fact is perhaps the most surprising result of the analysis of the experimental work.

The author would like to express his gratitude to Mr. Robert Heikes and Mr. Ronald Sladek for assistance in making the measurements, and to Dr. Zener for numerous suggestions and discussions.

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[7] C. Wert, J. App. Phys. **20**, 943 (1949). C. Zener, J. App. Phys. **20**, 950 (1949).

[8] J. K. Stanley, J. Metals **1**, 752 (1949).

[9] G. Richter, Ann. d. Physik **32**, 683 (1938).