# Interstitial Atomic Diffusion Coefficients*

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(Received April 19, 1949)

An attempt is made to interpret the temperature independent factor $D_0$ of the previously determined diffusion coefficients of interstitial solute atoms in metals. The primary uncertainty in the value of $D_0$ given by the standard reaction rate theory resides in an entropy factor $\exp(\Delta S/R)$. When cognizance is taken of an additional strain in the lattice surrounding a solute atom as it passes over a potential energy divide, and of the increase in entropy associated with an increase in lattice strain energy, one can estimate a "theoretical" range within which these entropy factors should lie. All past observations except for C and N in $\alpha-$Fe are consistent with this theoretical range. The $D_0$'s for these two systems were, therefore, redetermined by more precise measurements, and are found to be an order of magnitude higher than the original values. The associated entropy factors are consistent with the theoretical range.

## I. INTRODUCTION AND RESULTS

THE mechanism of diffusion of interstitial solute atoms in solid solution is well understood. The solute atoms diffuse by simply jumping between interstitial positions, the direction of each particular jump being random. The purpose of the present paper is to see how well the theoretical diffusion rate based upon this simple model and the observed diffusion rates can be brought into quantitative agreement.

The observed atomic diffusion coefficients are usually expressed in terms of two constants, $D_0$ and $E$, as follows:

$$D = D_0 e^{-E/RT}. \tag{1}$$

The theoretical diffusion coefficient for interstitial atoms in a cubic lattice has the form

$$D = \alpha a^2 / \tau. \tag{2}$$

Here $a$ is the lattice constant, $\tau$ is the mean time-of-stay in one interstitial position between jumps, and $\alpha$ is a numerical coefficient whose value depends upon the location of the interstitial positions. The values of $\alpha$ for face centered cubic (f.c.c.) and for body centered cubic (b.c.c.) lattices are computed in Section II and are listed in Table I. While our knowledge of the cohesive forces is not sufficient to permit an evaluation of the heat of activation $E$, the constant $D_0$ may be estimated fairly accurately. Towards this end one observes that, at least over a limited temperature range, the mean time-of-stay $\tau$ has a heat of activation, i.e.,

$$\tau^{-1} = \tau_0^{-1} e^{-E/RT}. \tag{3}$$

TABLE I. Diffusion constants.

| Lattice type | B.C.C. | F.C.C. |
|---|---|---|
| $\alpha$ | 1/24 | 1/12 |
| $n$ | 4 | 12 |

The "constant" $\tau_0^{-1}$ is found in Section II to be given by

$$\tau_0^{-1} = n v e^{\Delta S/R}. \tag{4}$$

In this equation $n$ is the number of nearest neighbor interstitial positions, $v$ is the frequency of vibration of a solute atom in an interstitial position, and $\Delta S$ is an entropy of excitation whose precise definition must be delayed until Section II. Corresponding to the interstitial positions being at the center of the unit cell and at the centers of the cube edges in a f.c.c. lattice, and at the center of the faces and edges of the unit cells in b.c.c. lattices,[1] the number of nearest neighbors is 12 and 4 for these two lattices, respectively. Upon comparing Eqs. (1)–(4), we obtain for $D_0$ the following theoretical equation

$$D_0 = n\alpha e^{\Delta S/R} a^2 v. \tag{5}$$

The only solution in which the constant $D_0$ has been measured accurately is that of carbon in $\gamma$-iron.[2] In the case of b.c.c. metals an alternative method is available for a test of the theoretical Eq. (4). In this method one studies the internal friction associated with the interstitial solute atoms, a type of internal friction which was first observed and correctly interpreted by Snoek.[1] From these internal friction measurements one finds directly the relaxation time $\tau_r$ for the establishment of an equilibrium distribution between the three types of interstitial positions, corresponding to the three principal axes along which the tetragonal axis of an interstitial position may lie. This relaxation time is equal to $1/\omega_m$, where $\omega_m$ is the angular frequency at which the internal friction is a maximum. It has been shown by Polder[3] that the time of relaxation $\tau_r$ is related to the mean time-of-stay $\tau$ by the relation

$$\tau = (\tfrac{3}{2})\tau_r. \tag{6}$$

From such internal friction measurements one may thus determine directly the mean time-of-stay $\tau$, and may

[1] J. Snoek, Physica 8, 711 (1941).
[2] C. Wells and R. Mehl, Trans. A.I.M.E. 140, 294 (1940).
[3] D. Polder, Philips Research Reports 1, 1 (1945).

TABLE II. Data relevant to diffusion.

| System | C in γ−Fe | C in α−Fe | | N in α−Fe | | C in T$_a$ | N in T$_a$ | O in T$_a$ |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | | Snoek,[a,b] Polder[c] | Present work | Snoek[a,b] | Present work | | | |
| $D_0$ (in cm /sec.) | 0.07[d] | 0.0005 | 0.008 | | 0.0014 | 0.0018 | 0.29 | 0.030 |
| $\tau_0^{-1}$ (in $10^{13}$ sec.$^{-1}$) | — | 1.5 | 23[e] | 0.29 | 3.7[e] | 4.2[f] | 640[g] | 66[f] |
| $E$ (in cal./mole) | 32,000[d] | 18,000 | 19,800 | 16,400 | 17,700 | 25,000 | 44,000 | 29,000 |
| $\nu$ (in $10^{13}$ sec.$^{-1}$) | 0.94 | 1.3 | 1.3 | 1.1 | 1.1 | 1.3 | 1.6 | 1.1 |
| exp($\Delta S/R$) | | | | | | | | |
|   "empirical" | 6 | 0.3 | 4 | 0.07 | 0.8 | 0.8 | 100 | 15 |
|   Theor. range | 1–60 | 1–13 | 1–13 | 1–13 | 1–10 | 1–10 | 1–64 | 1–16 |

[a] See reference 1.
[b] See reference 5.
[c] See reference 3.
[d] See reference 2.
[e] This paper.
[f] See reference 10.
[g] See reference 8.

thereby effect a comparison with theory through use of Eq. (4).

The theoretical expressions (4) and (5) for $\tau_0$ and for $D_0$ contain the factors $\nu$ and exp($\Delta S/R$), the numerical values of which are rather uncertain. An estimate of the vibration frequency $\nu$ will be obtained through the assumption that as a solute atom moves from one interstitial position to an adjacent interstitial position, its potential energy varies in a simple sinusoidal manner. Thus if $x$ is the coordinate along this path, we shall assume that

$$V(x) = (\tfrac{1}{2})E(1 - \cos 2\pi x/\lambda), \qquad (7)$$

where $E$ is the height of the potential barrier, which may be taken as approximately equal to the heat of activation, and $\lambda$ is the distance between the interstitial positions. The vibration frequency $\nu$ is then, according to this approximation, given by

$$\nu = (E/2m\lambda^2)^{\frac{1}{2}}. \qquad (8)$$

The values so calculated are given in Table II. As mentioned above, the interstitial positions in b.c.c. lattices have tetragonal rather than cubic symmetry, and hence the vibrations of solute atoms are not isotropic within these positions. Since the paths leading from any given interstitial position to each of its four nearest neighboring interstitial positions lie in a plane normal to the tetragonal axis, the frequency $\nu$ defined by Eq. (8) refers to the frequency of that component of vibration resolved upon this plane.

From a consideration of the fact that the lattice has more strain energy when a solute atom is midway between two interstitial positions than when it is at an interstitial position, and of the fact that strain energy reduces the local elastic moduli of the lattice,[4] we anticipate that $\Delta S$ will be positive, and hence the entropy factor to be greater than unity. Comparison between theory and experiment can, therefore, best be obtained by inserting the empirical values of $\tau_0^{-1}$ or of $D_0$ into Eqs. (4) or (5), respectively, and then, using the above estimated value of $\nu$, compute the entropy factor. The

"empirical" entropy factor so obtained should be greater than unity but should be less than that value which would correspond to all the heat of activation $E$ being in the form of lattice strain energy. This upper limit to the entropy factor is estimated in Section II.

The empirical values of the entropy factor, together with the theoretical range, are given in Table II. Only in the case of C in γ−Fe was $D_0$ determined directly from diffusion experiments. The value recorded refers to the limiting case of infinite dilution. The values of $D_0$ for C and N in α−Fe were deduced from magnetic measurements.[5] The values of $D_0$ for C, N and O in tantalum were obtained from internal friction measurements. When cognizance is taken of the fact that only a 2 percent error in the determination of $E$ changes the empirical value of the entropy factor by a factor of 2, it is seen that only in the case of C in α−Fe is there a serious discrepancy between the empirical entropy factor and its theoretical range. The attempt to resolve this discrepancy instigated the experimental work reported upon in Section III. As therein described, these experiments demonstrate that at the carbon concentrations (∼0.1 atomic percent) used, the jumping of the carbon atoms between adjacent interstitial positions cannot be described by a single time of relaxation, as was assumed in the original work. They further suggest that this anomalous behavior is due to the interaction of the solute atoms.

## II. ANALYSIS

We shall first evaluate for f.c.c. and for b.c.c. lattices the numerical coefficient $\alpha$ in Eq. (2). Since the diffusion coefficient is a scalar in cubic systems, it suffices to consider that the concentration gradient is parallel to a principal axis, which will be denoted as the $z$ axis. The plane $z = 0$ will be chosen as lying in a (001) plane of atoms. We then denote by $n(r,t)$ the number of interstitial atoms per unit area of the $r$'th (001) plane above $z = 0$. We shall further denote by $2\beta$ the probability that, when a solute atom jumps into a new interstitial

[4] C. Zener, Acta Cryst. 2, 163 (1949).

[5] J. L. Snoek, Physica 6, 591 (1939).

position, the jump will be into a new (001) plane. Then

$$n(r,t+\tau)=(1-2\beta)n(r,t)+\beta\{n(r+1,t)+n(r-1,t)\}.$$

If we now subtract $n(r,t)$ from both sides, and consider $n$ to vary only very slightly during a time interval $\tau$ or from one (001) plane to an adjacent (001) plane, we obtain

$$\partial n/\partial t=(\beta/\tau)\partial^2 n/\partial r^2.$$

In both f.c.c. and in b.c.c. lattices the (001) planes are spaced $\frac{1}{2}a$ apart, and hence the atomic diffusion coefficient is given by

$$D=\beta a^2/4\tau.$$

From a consideration of the spacing of the interstitial positions we readily see that $\beta$ is $\frac{1}{3}$ and $\frac{1}{6}$ for f.c.c. and b.c.c. lattices, respectively. We are thereby led to the values of $\alpha$ listed in Table I.

Since the jumping of a solute atom from one interstitial position to another may be regarded as one of the simplest examples of a rate process, it is natural to deduce the mean rate of jumping, $1/\tau$, from the standard rate theory developed by Eyring.[6] This theory gives

$$1/\tau=(nkT/h)P^*/P. \qquad (9)$$

Here $P^*$ is the partition function of the system of solute atom plus lattice, the solute atom being confined to move in a plane passing through the divide separating two interstitial positions, and oriented normal to the line joining the two interstitial positions. In the second partition function $P$ no restraint is placed upon the solute atom. The dominant part of $P$ will, therefore, arise from the region in the immediate vicinity of an interstitial position, where the forces may be regarded as harmonic. It is to be noted that $P$ refers to one more degree of freedom than does $P^*$.

In order to obtain a ratio of partition functions having the same number of degrees of freedom, we make the approximation of separating $P$ into two factors

$$P=P_v \cdot P_1^*,$$

where $P_v$ is the partition function for a single linear oscillator, and where $P_1^*$ is the partition function of the complete system with the solute atom constrained to move in a plane passing through an interstitial position. With this factoring of $P$ Eq. (9) becomes

$$1/\tau=(nkT/hP_v)e^{-\Delta F/RT}, \qquad (10)$$

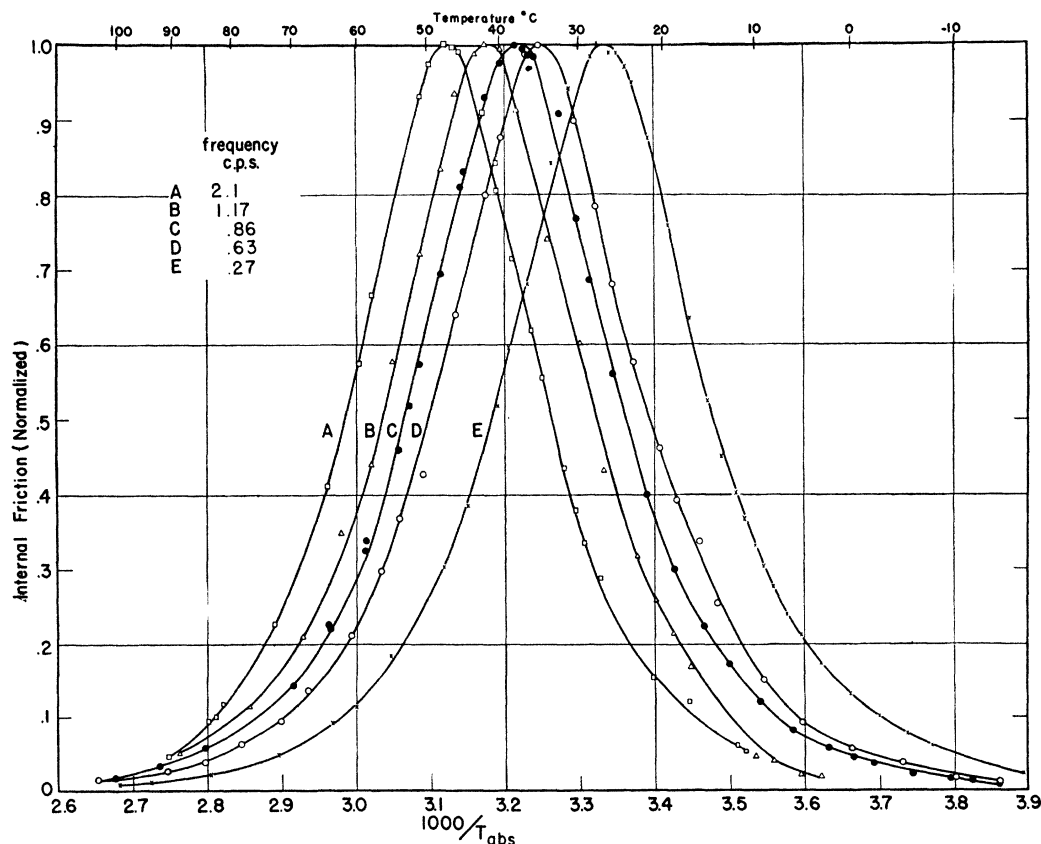where $\Delta F$ is the work required to transfer one gram



Fig. 1. Variation with temperature of internal friction of an iron specimen containing dissolved C at five frequencies of vibration.

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[6] H. Eyring, J. Chem. Phys. 3, 107 (1932); Glasstone, Laidler, and Eyring, The Theory of Rate Processes (McGraw-Hill Book Company, Inc., New York, 1941), pp. 184–191.
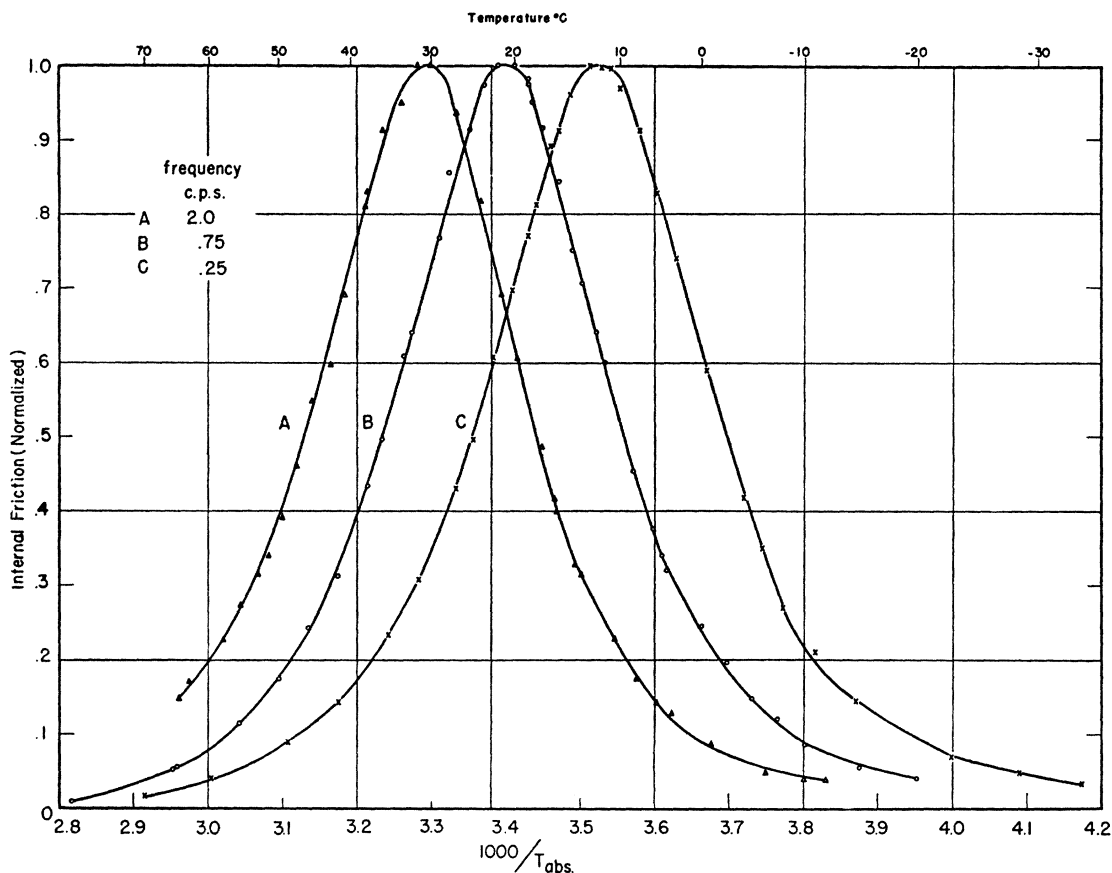
Fig. 2. Variation of internal friction with temperature for iron containing dissolved N.

mole of solute atoms from a constrained two-dimensional vibration about an interstitial position to a constrained two-dimensional vibration about a divide in a plane normal to the line joining the two neighboring interstitial positions.

Upon observing that

$$P_v^{-1} = 2 \sinh(h\nu/2kT), \qquad (11)$$

where $\nu$ is the frequency of vibration of the solute atom in an interstitial position, and upon observing that in the cases of interest in this paper only a slight error will be introduced by replacing $\sinh(h\nu/2kT)$ by its argument, we obtain

$$kT/hP_v = \nu. \qquad (12)$$

Even in the high degeneracy case of $h\nu/kT = 2$, an error of only 18 percent is introduced by the simplification of Eq. (12).

Upon combining Eq. (12) with Eq. (10) we obtain

$$1/\tau = n\nu e^{-\Delta F/RT}. \qquad (13)$$

This equation now reduces to Eqs. (3)–(4) when we write

$$\Delta F = \Delta E - T\Delta S,$$

where $\Delta E$ and $\Delta S$ have obvious interpretations, provided we can identify $\Delta E$ with the empirically defined "heat of activation" $E$. Now the "heat of activation" of $\tau^{-1}$ is defined by the equation

$$E = -Rd(\ln\tau^{-1})/d(1/T).$$

When this empirical definition is combined with the standard thermodynamic formula

$$\Delta E = d(\Delta F/T)/d(1/T),$$

the desired identity becomes apparent. It is to be particularly noted that this identity is valid whether or not $E$ is a function of temperature.

The approximation of Eq. (12) is seldom used in reaction rate theory. The authors wish to point out that by refraining from making this approximation one merely deludes oneself into thinking that quantum effects have been adequately taken care of. In the original derivation of Eq. (9) one considers the solute atom to behave in a classical manner in the vicinity of the divide with respect to the coordinate describing the position along a line joining two interstitial positions. Quantum effects are, therefore, not adequately taken account of by merely retaining the quantum expression for the partition function corresponding to a

vibration near a minimum in the potential energy. While the first-order quantum effects at the divide may be estimated by the method introduced by Wigner,[7] such a refinement would not be justified at the present time in view of the other uncertainties in the theory.

Our final task in this section is an estimation of the entropy factor $e^{\Delta S/R}$ in Eq. (4). Towards this end we set

$$\Delta S = -\partial \Delta F/\partial T.$$

If all the work $\Delta F$ went into straining the lattice, then $\Delta F$ would have essentially the same temperature coefficient as the elastic moduli. An upper limit to $\Delta S$ is thus obtained by setting

$$\Delta S \cong -E(d \ln\mu/dT),$$

where $\mu$ is the shear modulus. Upon taking the values $-0.00026$[8] and $-0.00020$[9] for the temperature coefficients $d \ln\mu/dT$ of iron and tantalum, respectively, one obtains the upper limits to the entropy factors given in Table II.

## III. EXPERIMENTS

The experimental work described in this section had as its aim the accurate determination of $\tau_0$ and $E$.

Once this was done, all the remaining empirical factors in Table II could be computed. For these measurements use was made of the internal friction peak arising from the stress induced redistribution in the three types of lattice sites of the interstitially dissolved atoms of C and N. It is well known that for an internal friction process involving a single relaxation time, the magnitude of the internal friction, $\Delta$, is given by

$$\Delta = 2\Delta_0/[(1/\tau_r\omega)+\tau_r\omega], \tag{14}$$

where $\Delta_0$ is the maximum magnitude of the internal friction. This maximum clearly occurs when the angular frequency, $\omega$, of the impressed stress is equal to the reciprocal of the relaxation time, $\tau_r$. While $\Delta_0$ is but a slowly varying function of temperature, $\tau_r$ in this instance is expected to vary rapidly with temperature according to the equation

$$\tau_r = \tau_{r0} \cdot \exp(E/RT). \tag{15}$$

The experimental work involved in the measurement of $\tau_{r0}$ and of $E$ in Eq. (15) was the measurement of $\Delta$ vs. temperature at a number of frequencies with C or N in solid solution in the iron specimen. The method of measuring $\Delta$ was the same as that used previously in this laboratory for such determinations.[8,10] The speci-
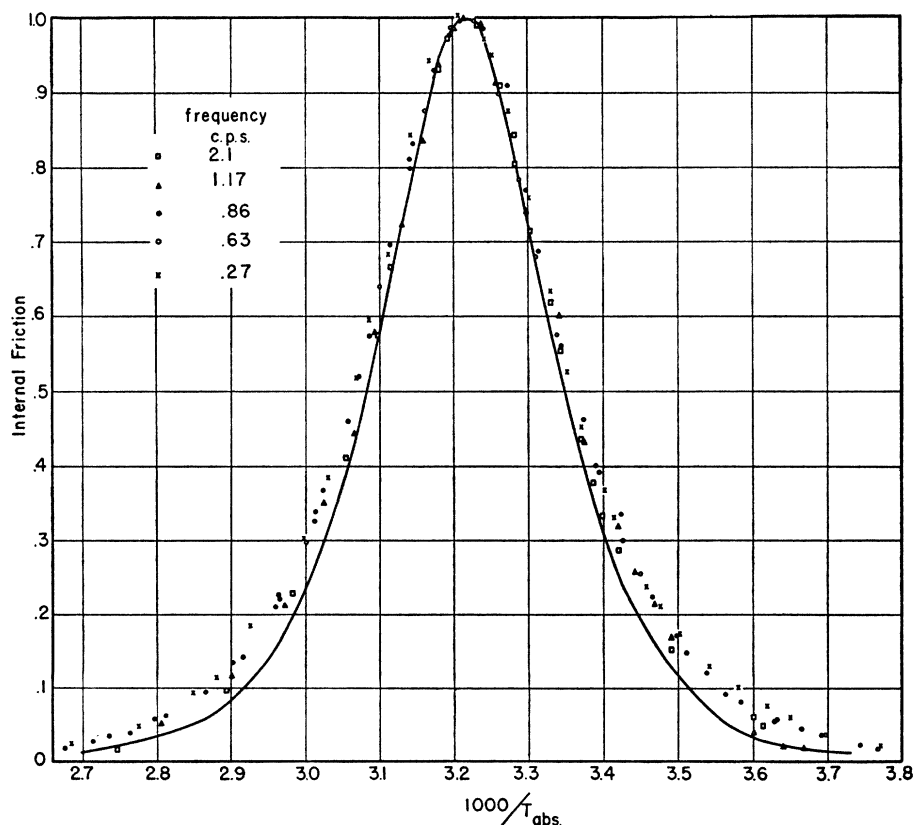


FIG. 3. Superposition of the internal friction peaks for C shown in Fig. 1. To avoid confusion about one-half of the points at the maxima of the curves shown in Fig. 1 have been omitted in this plot. The drawn curve is computed from Eqs. (14) and (15) with $E_C$ = 19,800 cal./mol.

| frequency c.p.s. | |
|---|---|
| □ | 2.1 |
| ▲ | 1.17 |
| ● | .86 |
| ○ | .63 |
| ■ | .27 |

Internal Friction

$1000/T_{abs.}$

[7] E. Wigner, Phys. Rev. 40, 749 (1932).
[8] T. S. Kê, Metals Tech. June, 1948, T.P. No. 2370.
[9] T. S. Kê, Phys. Rev. 74, 914 (1948).
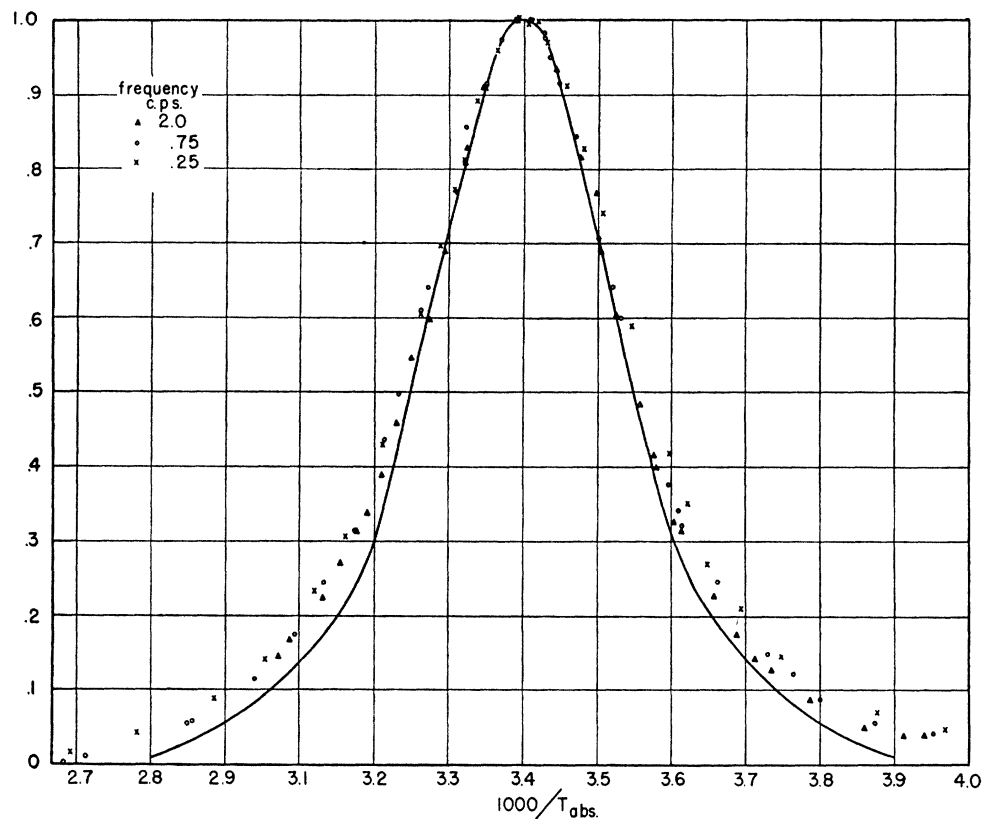[10] T. S. Kê, Phys. Rev. 74, 9 (1948).

Fig. 4. Superposition of the internal friction peaks for N shown in Fig. 2. The drawn curve is computed from Eqs. (14) and (15) with $\bar{E}_N$ = 1,7700 cal./mol.

men of iron was a wire 0.026 inch in diameter and about 1 foot long. This wire was made the suspension of a torsional pendulum; the inertia arm of which could be changed to give frequencies from $\frac{1}{4}$ to $2\frac{1}{4}$ c.p.s. The entire pendulum was suspended in an insulated double-walled vertical furnace. To obtain temperatures above room temperature, the furnace was heated electrically by windings outside the outer wall. To obtain low temperatures, air cooled by passage through liquid nitrogen was led through the chamber between the double walls. With this furnace, temperatures from $-30°C$ to $+200°C$ could be obtained. Since the internal friction varies rapidly with changing temperature (falling to less than $\frac{1}{2}$ the peak value $15°C$ off the peak), it is desirable to have the temperature uniform along the wire. Probing the furnace gave the information that over the section of the furnace used, at $200°C$ the temperature was uniform to $2°C$ and at $0°C$ to less than $1°C$. Details of the method of clamping the specimen and the technique of making the measurements of $\Delta$ are given by Kê.[8,10]

The specimens were prepared in the following manner: the iron wires were first cleaned of residual C and N by heating for several hours in an atmosphere of $H_2$ and water vapor at $720°C$. One of the wires was heated in a mixture of dry $H_2$ and n-heptane at $720°C$ for two hours to form a solid solution of about .015 percent C in $\alpha$-iron. The other wire was heated for three hours in a mixture of $H_2$ and $NH_3$ at $590°C$ to form a solid solution of about 0.015 percent N. After this treatment, the wires were quenched in cold water. With these low concentrations of solute, no observable precipitation from solid solution occurred during the measurements.

The actual measurement of the internal friction was then carried out at once. A specimen was mounted in the apparatus and the temperature was lowered to about $-35°C$. Gradually reducing the air flow allowed the temperature to rise to room temperature very slowly (about $1°C$ every five minutes). When the furnace reached room temperature, the air was turned off completely and the furnace was heated to $100°C$ in steps of a few degrees by gradually raising the furnace current. Measurements were made of the internal friction at intervals. Further measurements made at selected points with the temperature of the furnace falling again to room temperature gave data practically identical with that obtained with rising temperature. The temperature measurements themselves were made with an Al-Cr thermocouple placed near the center of the wire.

Measurements obtained for C and N at a number of frequencies are plotted in Figs. 1 and 2. These plots permit the immediate calculation of $E$ using an equation amply discussed elsewhere.[9]

$$E = -R \cdot \frac{d(\ln\omega)}{d(1/T)}\Bigg|_{\Delta=\text{const.}} \tag{16}$$

To determine $E$ from Figs. 1 and 2, plots were made of $\ln\nu$ vs. $1/T$ at $\Delta/\Delta_{max}=0.1$, $\Delta/\Delta_{max}=0.2$ etc., for both sides of the internal friction peak. While each set of points lay on a straight line, the slopes of these lines showed a consistent variation, increasing slightly in passing from the extreme left to the extreme right side of the internal friction curve. The average of these slopes was substituted into Eq. (16), yielding for the effective heats of activation $E_C$ the value $19,800\pm400$ and for $E_N$ the value $17,700\pm400$ cal/mole. From these values of $E$ and from an observation of $\tau_{r0}$, the position of the maximum at a given frequency, the value of $\tau_0$ was computed. For nitrogen $\tau_{r0}$ is determined to be $1.8\times10^{-14}$ sec., hence $\tau_0^{-1}$ in Table II is $4\times10^{13}$ sec.$^{-1}$. For carbon $\tau_{r0}$ is $2.92\times10^{-15}$ sec., hence $\tau_0^{-1}$ is $2.3\times10^{14}$ sec.$^{-1}$. It is to be observed that the estimated errors in the determination of $E$ lead to large errors in the determination of $\tau_0^{-1}$ and hence in the calculation of $D_0$ and $e^{\Delta S/R}$. Thus $D_0$ and $e^{\Delta S/R}$ are possibly in error by a factor of 2.

The values of $E_C$ and of $E_N$ previously determined by Snoek[1] were significantly smaller, being 18,000 and 16,200, respectively, and hence led to estimated values of $D_0$ about 10 times smaller than those estimated from our experiments. Snoek determined these values originally by magnetic relaxation measurements, and later found these values to be in fair agreement with his internal friction measurements, but stated that slightly higher values would have been in better agreement.

If the internal friction were accurately described by Eqs. (14) and (15), then on a plot of $\Delta$ vs. $1/T$ it should be possible to superpose all the curves by shifting them on the $1/T$ axis. Further, all the curves should fit a curve computed using Eq. (15) with a value for $E$ as determined above. Such plots are shown in Figs. 3 and 4. It is seen that for both C and N the experimental points lie significantly outside the computed curves. This slight excess in the breadth of the experimental curves over that of the theoretical curve finds a ready interpretation in a possible slight dispersion of relaxation times. Such a dispersion would indicate that all the interstitial positions were not quite energetically equivalent, and hence either that the lattice contains imperfections, or that the solute atoms interact with one another. This interpretation is strengthened by the observation that the experimental curves lie closer to the theoretical curve the higher the frequency of vibration, and hence the higher the average temperature during a run. A higher temperature will reduce any tendency of the solute atoms to cluster about lattice imperfections or about one another. The same type of discrepancy between the experimental and ideal single relaxation-time internal friction curves were found by Kê[8,10] in his study of C, N and O in tantalum. It is interesting to observe that the order C, N and O is both the order for an increasing discrepancy and for an increase in concentration, as measured by the peak in the internal friction curve. This coincidence indicates that, at least in tantalum, interaction between solute atoms is responsible for the discrepancy, rather than lattice imperfections. Such an interaction is consistent with the strong attraction between interstitial solute atoms in b.c.c. lattices found by one of the authors.[11]

[11] C. Zener, Phys. Rev. 74, 634 (1948).