Diffusion in Copper and Copper Alloys

Part I. Volume and Surface Self-Diffusion in Copper

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A survey, comparison, and critical analysis is presented of data compiled from the scientific literature concerning copper self-diffusion. Topics include volume diffusion, dislocation pipe diffusion, surface diffusion, sintering, electromigration, thermomigration, pressure effect on diffusion, strain-enhanced diffusion, nuclear magnetic resonance measurements of solid state diffusion and diffusion in molten copper. An extensive bibliography is presented along with figures, tabular presentation of data, and discussion of results.

Key words: Copper; diffusion; electromigration; liquid copper diffusion; nuclear magnetic resonance and diffusion; pressure effects on diffusion; self-diffusion; sintering; surface diffusion; thermomigration.

Contents

1. Introduction

Copper and copper alloys are important commercial materials which often are used at temperatures where diffusion processes strongly affect their properties. Significant changes in mechanical and electrical properties can occur through surface alloying, compositional changes at interfaces, and interface degradation resulting directly from diffusion. Many metallurgical processes such as creep, precipitation, ageing, and corrosion are diffusion-limited. Other important diffusion effects include homogenization of alloys, electromigration effects on copper components in electrical circuits, diffusional breakdown of protective films, permeability of thin-walled tubing, and diffusion bonding.

Because of the strong practical and scientific interest in diffusion involving copper and its alloys, references to this topic in the literature are very numerous. In view of the large body of data to be reported, it is convenient for present purposes to review this subject in several parts. Copper self-diffusion is treated in this first part. Attention is focused on copper diffusion itself, rather than on formation and annealing of crystal defects. Also, emphasis is on the direct experimental results, with diffusion theory being discussed only where it aids in selecting among conflicting data or in predicting and interpreting experimental results.

The primary quantities of interest for diffusion are the diffusion coefficient, D, and the activation energy for diffusion, Q. The diffusion coefficient is defined by the equation

$$J = -D(\partial c/\partial x), \tag{1}$$

where $\partial c/\partial x$ is the concentration gradient of the diffusing species along a direction (x) of interest and the diffusion flux, J, is the amount of diffusing species crossing unit area normal to the x-axis per unit time. D itself is a constant of proportionality and usually is expressed in units of cm^2/s. Experimentally, D is usually found to depend exponentially on temperature according to an Arrhenius type equation,

$$D = D_0 \exp(-Q/RT). \tag{2}$$

Thus, a straight line is usually obtained when log D is plotted as a function of T^{-1}. Here T is the absolute temperature, D_0 and Q are experimentally measured constants which can be determined from the intercept and the slope of that line, and R is the universal gas constant (1.987 cal K^{-1} mol^{-1} = 8.314 $J \cdot K^{-1} \cdot mol^{-1}$).

The quantity Q in eq (2) is usually found expressed in the literature in units of kcal/mol, or in units of kcal alone (with the mole understood). Usually Q can be determined to only two or three significant figures and has a value between 10,000 and 100,000 cal/mol. Thus, when Q is expressed directly in terms of cal/mol, as is sometimes found in the literature, the last few zeros before the decimal are not significant figures. A second type of unit for Q frequently found in the literature is the electron volt or electron volt per atom. When this unit is reported, it is understood that R in eq (2) is replaced by Boltzmann's constant k (equal to 1.3806×10^{-23} $J \cdot K^{-1}$ or 8.617×10^{-5} $eV \cdot K^{-1}$).

One fundamental distinction which can be made between different types of diffusion measurements is that between volume diffusion, where atoms move through parts of the material having regular crystal structure, and short circuit diffusion processes, where the atoms move along easier diffusion paths such as surfaces, grain boundaries or dislocations. Both types of data are collected in the present review.

Volume diffusion normally is found to have an appreciably higher activation energy than short circuit diffusion; but, because of the many volume diffusion paths available, volume diffusion normally dominates at high temperatures. Short circuit diffusion usually becomes the predominant means of mass transport at lower temperatures, however. Since copper has a face-centered cubic structure, volume diffusion in copper is isotropic, and D is independent of the diffusion direction. By contrast, surface diffusion and other types of short circuit diffusion should not be expected to be isotropic, since the surface structure and particular directions of easy diffusion paths can introduce significant anisotropic effects. Grain boundary diffusion may be significant in polycrystalline material and tends to increase the net measured diffusion, especially when measurements are made at temperatures below $(2/3)T_m$, where T_m is the melting point. For this reason, single crystal results are considered more reliable as measurements of volume diffusion.

The most accurate method of measuring volume diffusion is by radioactive-tracer-sectioning techniques. Here a thin layer of radioactive tracer atoms is deposited on the surface of a homogeneous crystal and diffusion is allowed to proceed for time t. The specimen is then sectioned into slices parallel to the surface and the specific activity, c, of each slice is measured. When D is independent of time, as is expected if temperature, pressure and composition are held constant, solution of eq (1) after application of the continuity relation $\partial J/\partial x = -\partial c/\partial t$ yields

$$c = c_0 \exp(-x^2/4Dt), \tag{3}$$

where c_0 is a constant and x is the distance of the slice from the surface. When a plot of experimental c values as a function of x^2 yields a straight line, it is presumed that D indeed is constant and D is calculated from the slope of this line.

The tracer-sectioning method can yield results which are reproducible to within a few percent. In practice, however, this accuracy is not always obtained. For example, contributions from fast-diffusing contaminants in the tracer, short circuit diffusion, specimen misalignment, and uniform loss of material all may affect the measured c values and would tend to yield apparent D values which are too large. Errors in temperature measurement also may be important but such errors could either increase or decrease apparent D values. Further details on problems encountered in measuring volume diffusion and on methods of measurement may be found in general references, such as those of Tomizuka [1, 2][1] and Lundy [3], which discuss experimental volume diffusion techniques.

Because of the accuracy of tracer techniques, such results are emphasized in this review wherever possible. However, results applicable to volume diffusion from other methods such as nuclear magnetic resonance and sintering also are reviewed. Other volume diffusion phenomena which are discussed include diffusion in an electric field (electromigration), diffusion in a temperature gradient (thermomigration), effects from hydrostatic pressure, diffusion in strained crystals, and self-diffusion in molten copper.

In choosing among various tracer results for reliability, the internal consistency and reproducibility of the data are considered important. It is expected that the experimental points, expressed as log D, should fall very nearly on a straight line when plotted as a function of T^{-1}, as given by eq (2). The degree of scatter from a line drawn through the experimental points is usually assumed to provide a good indication of the accuracy of the data. Such a line usually will not be well-established if only a few measurements in a limited temperature range are reported. For this reason, data taken at many different temperatures and over a wide temperature range usually are considered more useful and are more easily evaluated.

Diffusion of copper on copper surfaces can be measured by measuring the change in shape of the copper surface or by introducing radioactive tracer atoms on the surface. In both cases, possible volume diffusion effects on the results must be taken into account. The surface diffusion coefficient, D_s, is defined from eq (1) but with the change that c is concentration per unit area and J represents flux across a line on the surface normal to the flux. Reviews of experimental surface diffusion techniques have been given by Blakely [4], Neumann and Neumann [5], Gjostein [6–9], and Bonzel [10].

In contrast to the numerous surface self-diffusion measurements reported on copper, grain boundary self-diffusion in copper appears to have been little measured. This relative lack of grain boundary self-diffusion measurements probably arises because methods involving changes in morphology are not easily applied to grain boundary diffusion (mainly sintering and pore shrinkage studies) and also because the short half-lives of radioactive copper isotopes make it difficult to perform the long-duration diffusion runs which are needed to measure grain boundary diffusion as a quantity separate from volume diffusion by tracer techniques. Similar problems arise in measuring diffusion along the easy path provided by dislocations (dislocation pipe diffusion).

An important class of diffusion measurements are those involving diffusion under various driving forces, such as described in the sections on electromigration and thermomigration. Because of the driving forces, an additional term is required in the diffusion equation. Under a driving force eq (1) can be written as

$$J = -D^*(\partial c/\partial x) + \langle v \rangle_F c, \tag{4}$$

where D^* is the tracer diffusion coefficient which appears in eq (3) and $\langle v \rangle_F$ is the atom drift velocity from driving

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[1] Numbers in brackets indicate the literature references.

forces. In general,

$$\langle v\rangle_F=\frac{D^*F}{\psi kT}, \tag{5}$$

where F is the physical driving force exerted on individual diffusing atoms and ψ is a numerical factor dependent on lattice geometry and the atom jump frequency ratios. For self-diffusion, ψ equals the correlation factor, f, for self-diffusion. For volume diffusion by a vacancy mechanism in a face-centered cubic crystal, as found for copper, the correlation factor equals 0.7815. For volume self-diffusion via divacancies, f equals 0.458.

Equation (5) is frequently used in determinations of surface diffusion coefficients. When this is done, the surface forces, F, customarily are evaluated independently and the correlation factor, f, is assumed equal to unity. Since it is believed that surface diffusion occurs mainly by motion of adatoms across the surface, this value of f for surface diffusion appears reasonable.

When the force in eq (5) arises from an electric field E, as in electromigration,

$$F=q^*E, \tag{6}$$

where q^* is called the effective charge of the diffusing entity. When the force arises from a temperature gradient $\partial T/\partial x$, as in thermomigration, one can define

$$F=\frac{-Q^{**}\psi}{T}\frac{\partial T}{\partial x}, \tag{7}$$

where Q^{**} is the measured heat of transport. Writing eq (7) in this form with ψ included in the expression for F actually provides a simplification in reporting experimental results, since then ψ does not enter into the determination of Q^{**} from measurements of $\langle v\rangle_F$. However, the basic atomic heat of transport, Q^*, equal to the ratio of the heat flux to the atom flux, does not equal Q^{**} but instead equals $Q^{**}\psi$.

In determining $\langle v\rangle_F$ and hence F, investigators may measure a profile displacement directly or, for self-diffusion, may determine the velocity of a marker on a specimen surface. The latter approach assumes that the marker velocity results from volume diffusion of atoms across the marker plane, with the apparent marker motion being in a direction opposite to the atom flux.

2. Cu*→Cu (Volume Diffusion)

2.1. High Temperature Range

Self-diffusion in copper has been measured by many different investigators. A selection from the more recent and apparently most reliable data is presented in figure 1. In this figure, the solid line represents the equation,

$$D=0.78 \exp\,(-50.5 \text{ kcal mol}^{-1}/RT) \text{ cm}^2/\text{s},$$

which is quoted by Rothman and Peterson [11] as providing the best least squares fit to their data, measured in the temperature range 700 to 1060 °C. The experiments of Rothman and Peterson were done on copper single crystals mainly with purified copper-67 tracer (62.2 hour half-life) and with the diffusion temperatures measured to ±1 °C. In view of the careful serial sectioning and counting techniques used, these results are probably very accurate. The scatter in these data yields a very small statistical uncertainty in the activation energy, $Q=50.5\pm0.2$ kcal $\text{mol}^{-1}=2.19\pm0.01$ eV.

The other data shown in figure 1 agree very well with that of Rothman and Peterson in the high temperature range (870 to 1060 °C). Below 870 °C a small discrepancy begins to appear which grows to more than 20 percent below 750 °C. The results of Kuper, Letaw, Slifkin, Sonder, and Tomizuka [12] are in very good agreement with those of Beyeler and Adda [13, 14], but at the lower temperatures both of these results show D values which are appreciably larger than those of Rothman and Peterson. The measurements by Kuper et al. and by Beyeler and Adda were done on single crystals by serial-sectioning, radioactive-tracer methods similar to those of Rothman and Peterson, the only indicated difference being that the tracer copper-64 (12.8 hour half-life) was used. Since the difference in isotope used should not greatly affect the results, the discrepancy at temperatures below 750 °C still is not explained.

Rothman and Peterson [11, 15] diffused copper-64 and copper-67 simultaneously into the same specimen in order to obtain isotope effect measurements. Measurements were made at five different temperatures in the range 894 to 1061 °C. They found less than a 2 percent difference in diffusion coefficient, $(D_{64}-D_{67})/D_{64}=0.0155\pm0.0007$ with no systematic dependence on temperature. In separate diffusion experiments using copper-64 at 702 and 786 °C, where effects from diffusion along short-circuiting fast-diffusion paths or from the short half-life of the copper-64 tracer might be especially important, their results from copper-64 were 5 or 10 percent larger than their copper-67 results, which were determined from longer-duration diffusion runs. This difference is larger than the $1\frac{1}{2}$ percent effect obtained in the conventional isotope effect experiments reported above but still does not equal the discrepancy between the Rothman-Peterson diffusion coefficient values and those measured by other investigators at these temperatures.

It may be noted that the activation energy and pre-exponential factor for the Arrhenius equation that fit the data of Kuper et al. ($Q=47.12\pm0.33$ kcal/mol, $D_0=0.20\pm0.03$ cm²/s, $T=685$–1063 °C) agree remarkably well with those values that fit the data of Beyeler and Adda ($Q=46.9$ kcal/mol, $D_0=0.18$ cm²/s, $T=650$–990 °C). Nevertheless, errors which affect diffusion measurements more frequently result in measured D values that are too high rather than too low, especially at lower temperatures. Thus, when two sets of data appear equally self-consistent, those reporting the smaller diffusion coefficients are more frequently correct. In the present case, the Arrhenius equation given by Rothman and Peterson probably is the best choice to describe volume diffusion in the range 700 to 1060 °C.

As part of a broad investigation of diffusion in copper-nickel-zinc alloys, Anusavice and DeHoff [16] measured diffusion of copper-67 tracer in pure polycrystalline copper

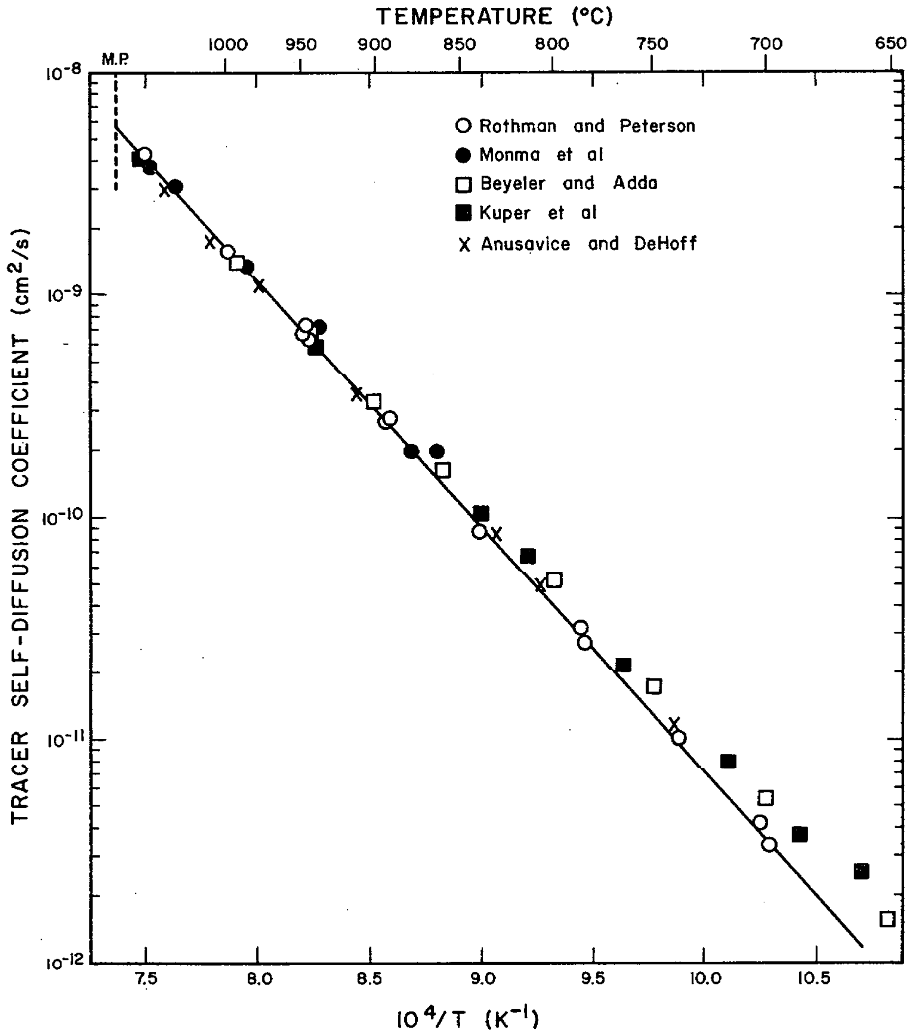

FIGURE 1. Copper self-diffusion in solid copper above 650 °C.

The solid line is that fitting the data of Rothman and Peterson [11] with $Q=50.5$ kcal/mol and $D_0=0.78$ cm^2/s.

in the temperature range 740 to 1045 °C by serial-sectioning techniques. The measurements below 850 °C yielded diffusion coefficients which were approximately midway between those measured by Kuper et al. and by Rothman and Peterson (see fig. 1). Similarly, the activation energy quoted by the authors had an intermediate value (48.3 kcal/mol) compared to the above investigations. At the highest temperatures, the diffusion coefficients measured by Anusavice and DeHoff were actually smaller than those of Rothman and Peterson, but the average agreement is good.

Tracer-sectioning measurements by Monma, Suto, and Oikawa [17] for copper-64 diffusing in polycrystalline copper also agree rather well with the data described above, as shown in figure 1. Since these experiments were done at high temperatures (863 to 1057 °C) where volume diffusion occurs easily, it is reasonable that fast diffusion along the grain boundaries would not appreciably affect the results.

A number of other tracer measurements of self-diffusion in copper also have been made, mostly on polycrystals and always with copper-64 as the tracer. The D values from these measurements often have differed by factors of two or more from those shown in figure 1. These results are not shown on figure 1 but instead are summarized below.

The first copper tracer measurements were reported in 1939 by Rollin [18], who used serial sectioning to measure diffusion of a 0.1 mm thick surface layer made radioactive by deuteron bombardment of a cylindrical block of copper. Soon thereafter, measurements were also reported by Steigman, Shockley, and Nix [19] and by Raynor, Thomassen, and Rouse [20]. These investigators determined D values from the decrease of measured surface activity resulting from diffusion of copper layers containing copper-64 which had been electroplated on the surface of a copper polycrystal. In all of these sets of data, D values at only three temperatures were measured so that activation energies were not well established. The D measurements of Raynor, Thomassen, and Rouse were consistently a factor of 2 or 3 higher than those shown in figure 1. By contrast, those of Rollin were lower than those in figure 1 by a factor of 2 except at the highest temperature. The results of Steigman, Shockley, and Nix provided a range of possible values at each temperature of ±25 to 40 percent but did include the figure 1 values within this range. Maier and Nelson [21] in 1942 carried out a more thorough investigation using both polycrystal and single crystal copper specimens. The serial sectioning analysis technique was followed. The resulting D's in all cases were larger than those shown in figure 1 usually by about 50 percent. All this early work appears lacking in accuracy and self-consistency compared with the more recent work shown in figure 1 and should be considered as superseded.

Recent work by Kučera and Million [22, 23] using copper polycrystals (mean grain size 2.3 mm) and a residual activity method of measurement also yielded D values noticeably higher than given by the solid line in figure 1, the difference being about 20 percent over their entire range from 800 to 1040 °C.

Mercer and co-workers [24] reported a series of experiments in which a copper alloy foil was sandwiched between two bulk specimens of pure copper. The alloying constituent (either zinc, silver, cadmium, or cobalt) and the copper in the foil, which both had been rendered radioactive by a reactor-radiation prior to formation of the couple, diffused symmetrically into the two bulk copper specimens and diffusion coefficients were calculated from the resulting Gaussian penetration profiles. The alloying (less than 1% impurity) present in these experiments at the original foil position and the resulting chemical concentration gradient in this region would cause deviations from pure self-diffusion. Nevertheless, values of D^*_{Cu} which agree well with those shown in figure 1 were obtained by this approach, with $Q=49.56\pm0.30$ kcal/mol and $D_0=0.62\pm0.025$ cm^2/s being quoted by Mercer as summarizing these results for the temperature range 854 to 1066 °C.

2.2. Low Temperature Range—Possible Curvature in log D vs T^{-1} Plot.

Mehrer and Seeger [25–27] have analyzed the temperature dependence of the copper tracer self-diffusion coefficients measured by Rothman and Peterson [11]. They find that there is a slight upward curvature in a plot of these values on a log D versus T^{-1} plot, and they interpret this curvature as arising partly from divacancies becoming more important at the higher temperatures and partly from a temperature dependence in the enthalpy and entropy of activation. Thus, in the usual case where the divacancy binding energy, $E_{2v}{}^B$, is less than the energy of formation of monovacancies, the ratio of divacancies to monovacancies increases with temperature. Mehrer and Seeger's calculations yield for self-diffusion in copper

$$D^*=D_{m0}T^{1/2}\exp\left(-Q_m/kT\right)+D_{d0}T^{1/2}\exp\left(-Q_d/kT\right),$$

where subscript m refers to monovacancies and subscript d to divacancies with $Q_m=2.07$ eV $-$ 47.7 kcal mol^{-1}, $D_{m0}=5.77\times10^{-3}$ cm^{2}s$^{-1}K^{-1/2}$, $Q_d=2.58$ eV $=59.4$ kcal mol^{-1}, $D_{d0}=161.5\times10^{-3}$ cm^{2}s$^{-1}K^{-1/2}$, and $E_{2v}{}^B=0.12$ eV.

With this interpretation, the portion of D^* arising from divacancies is 25 percent at 1060 °C and decreases to 6 percent at 700 °C. These temperatures are at the two ends of the temperature range covered by Rothman and Peterson. It may be noted that the activation energy Q_m calculated for monovacancies is almost 3 kcal/mol smaller than the overall value $Q=50.5$ kcal/mol measured by Rothman and Peterson. The majority of this difference results from inclusion of the divacancy term in the above equation. The temperature dependence from the $T^{1/2}$ factors, which arise from assuming temperature dependent entropy terms, is equivalent to that from an increase in activation energy of about 1 kcal/mol when applied to the temperature range of Rothman and Peterson's data.

If one extrapolates high temperature measurements of diffusion coefficients to estimate diffusion coefficients at lower temperatures, the equation above which includes divacancy contributions will yield significantly higher D^* values than will the single Arrhenius equation given by Rothman and Peterson. This occurs because the dominant term at lower temperatures, associated with monovacancy diffusion, is governed by the smaller activation energy, $Q_m=47.7$ kcal/mol. For extrapolation purposes, accurate calculations of divacancy contributions at high temperatures may be important.

Wynblatt [28] performed a divacancy analysis which was similar to, but somewhat simpler than, that of Mehrer and Seeger, since he did not include a temperature dependence in the activation entropy or enthalpy. Wynblatt applied his equations not only to the experimental values of Rothman and Peterson but also to those of Kuper et al. [12] and Beyeler and Adda [13]. He found that the results for comparative activation energies and D_0 values for monovacancies and divacancies depended strongly on which set of experimental data was used, and he concluded that these statistical analyses provided only an insensitive means of determining Q_d-Q_m and D_{do}/D_{mo}. The presence of large uncertainties in the values of the divacancy parameters as calculated by Mehrer and Seeger has also been emphasized by Burton and Froozan [29], who in addition propose a different type of statistical analysis.

To check these theories, only limited experimental results are available. Recent preliminary tracer measurements by Lam and Rothman [30] in the temperature range 340 to 380 °C indicate values similar to those predicted by Mehrer and Seeger (within ±40%). These experimental results are 2 to 4 times larger than those predicted from straight line extrapolation of Rothman and Peterson's high temperature results and at the lowest temperatures are a factor of 2 smaller than might have been predicted from extrapolation of the high temperature results of Kuper et al. or Beyeler and Adda.

Mortlock [31] used a chemical micro-sectioning technique to remove very thin layers (averaging 400 Å in thickness) after tracer self-diffusion in pure copper for 5 hours at 523 °C. When the fraction of radioactivity remaining in the specimen was plotted as a function of the cumulative thickness of specimen removed, three distinct diffusion regions were found within 1 μm of the free surface, with the apparent diffusion coefficient being larger for the regions farther into the specimen. No diffusion coefficients were quoted, however.[2]

Estimates of the low temperature volume self-diffusion coefficients in copper also have been obtained by Bowden and Balluffi [32] from the rate of shrinkage of voids measured by transmission electron microscopy in quenched pure copper specimens. Their measurements were done in the temperature range 390 to 560 °C, and in general agree with extrapolation of the high temperature tracer self-diffusion measurements in pure copper, but with large possible errors. The results lie above the extrapolation of an Arrhenius line based on $Q=50.5$ kcal mol^{-1} as measured by Rothman and Peterson [11] but lie in the general range of extrapolation of lines based on either $Q=47\pm0.1$ kcal mol^{-1} determined by Kuper et al. [12] and Beyeler and Adda [13] or $Q=47.7$ kcal mol^{-1} determined by Mehrer and Seeger [25] for the monovacancy term in their reanalysis of Rothman and Peterson's data.

In summary, the low temperature measurements of volume self-diffusion in copper all seem to lie appreciably above extrapolations of the straight line shown on figure 1. As discussed earlier, this line is believed to represent the most reliable data for diffusion at high temperatures (above 700 °C). Analysis of the possible curvature which should appear in this line leads one to expect D^* values at lower temperatures (around 400 °C) which are higher by approximately a factor of two than the straight line extrapolation.[3]

3. Dislocation Pipe Diffusion

Bowden and Balluffi [32] compared the shrinkage rate of voids in pure copper which were connected to a free surface by a dislocation to the shrinkage rate of voids which were not so connected. Even at their lowest annealing temperature of 390 °C, they found no effect from the dislocation. They concluded that the dislocation pipe diffusion coefficient at 390 °C must be less than 4×10^{-13} cm^2/s, assuming a pipe radius of five atomic distances. From comparison with similar measurements on aluminum crystals, Bowden and Balluffi concluded that dislocation pipe diffusion is slower relative to bulk diffusion in copper than in aluminum.

As part of a general review of fast diffusion down dislocations in fcc metals, Balluffi [33] estimated values of self-diffusion in the fast diffusion regions (the "dislocation pipes") near dislocations in pure copper. His estimate was based on measurements of germanium diffusion in copper. He again suggests that copper is a slow-diffuser in dislocation pipes and estimates that $A_dD_d\approx10^{-16}$ exp $(-1.53\ \mathrm{eV}/kT)$ cm^{4}s^{-1} in the temperature range $T\approx210$ to 350 °C, where A_d is the dislocation pipe area (taken here to be 2.5×10^{-15} cm^2) and D_d is the diffusion coefficient in this area. At these temperatures, expressed in terms of T/T_m where T_m is the melting point of the metal under consideration, these estimated values of A_dD_d in copper are two or more orders of magnitude smaller than comparable measured values for aluminum self-diffusion.

4. Surface Diffusion

The diffusion coefficients and activation energies reported in the literature for copper surface self-diffusion often are in serious disagreement. Reported activation energies differ by a factor of two or more, with the D values themselves sometimes differing by two orders of magnitude. Two main factors seem to be the sources of this disagreement. (1) The measured surface diffusion values depend strongly on the atmosphere in which diffusion takes place. Diffusion occurs much more readily in an oxygen atmosphere or in vacuum than in a hydrogen atmosphere. This effect probably arises from the influence that surface impurities can have on the diffusion process. Oxygen may remove the inhibiting effect of impurities or possibly may form complexes which actively aid diffusion. (2) At high temperatures (above say 970 °C), an additional diffusion mechanism with higher activation energy appears to contribute significantly to surface diffusion. Measurements which include higher temperature points tend to report higher activation energies.

Most surface diffusion measurements have been made by observing the changes that surface diffusion causes in surface topography. Here the tendency to minimize surface energy provides the driving force for diffusion, as in grain boundary grooving experiments or in the topographically opposite phenomenon of thermal smoothing of surface features, such as scratches introduced on the surfaces.

Gjostein [34] and Bonzel and Gjostein [35–37] made a number of measurements of thermal smoothing of surface scratches on copper using laser diffraction and interferometric techniques. They conclude that the measurements most characteristic of true surface diffusion are those for a near vacuum with a slight oxygen atmosphere, assuming that the oxygen acts to remove impurities which inhibit diffusion. In the temperature range 500–960 °C, their data, which were obtained from measurements on (110) surfaces, can be represented by [9, 10]

$$D_s=0.26\ \exp\ (-20.7\ \mathrm{kcal\ mol^{-1}}/RT)\ \mathrm{cm^2/s}.$$

From 1000 °C to the melting point (1083 °C), a much larger activation energy (approximately 63 kcal/mol) was found, with D_s at the melting point extrapolated to be about 5×10^{-4} cm^2/s. (See figure 2.)

In their hydrogen atmosphere measurements, Bonzel and Gjostein found lower D_s values, ranging from 10^{-4}

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[2] In a more recent publication [Mortlock, A. J., and Price, D. M., "Measurement of Lattice Diffusion in Copper at Relatively Low Temperatures," Metall. Trans. 4, 363–364 (1973)], Mortlock and Price report similar measurements on a number of specimens in the temperature range 400 to 526 °C. Mortlock and Price calculate volume diffusion coefficients from the middle region and obtain results somewhat higher than extrapolations of the high temperature results. Diffusion coefficient values for Regions I and III also were estimated.

[3] Additional tracer-sectioning measurements of copper self-diffusion at low temperatures (301 to 632 °C) have recently been reported by Maier, Bassani, and Schüle. [Maier, K., "Self-Diffusion in Copper between 630 and 300 °C," Thesis, University of Stuttgart, (1973); Maier, K., Bassani, C., and Schüle, W., "Self-Diffusion in Copper between 359 and 632 °C," Phys. Lett. (in press)]. Very thin sections were obtained by sputtering techniques. Diffusion coefficients measured at twelve different temperatures between 392 and 632 °C agreed within ±10 percent with the equation of Mehrer and Seeger. Six other measurements at lower temperatures showed higher D^* values than those predicted by Mehrer and Seeger.

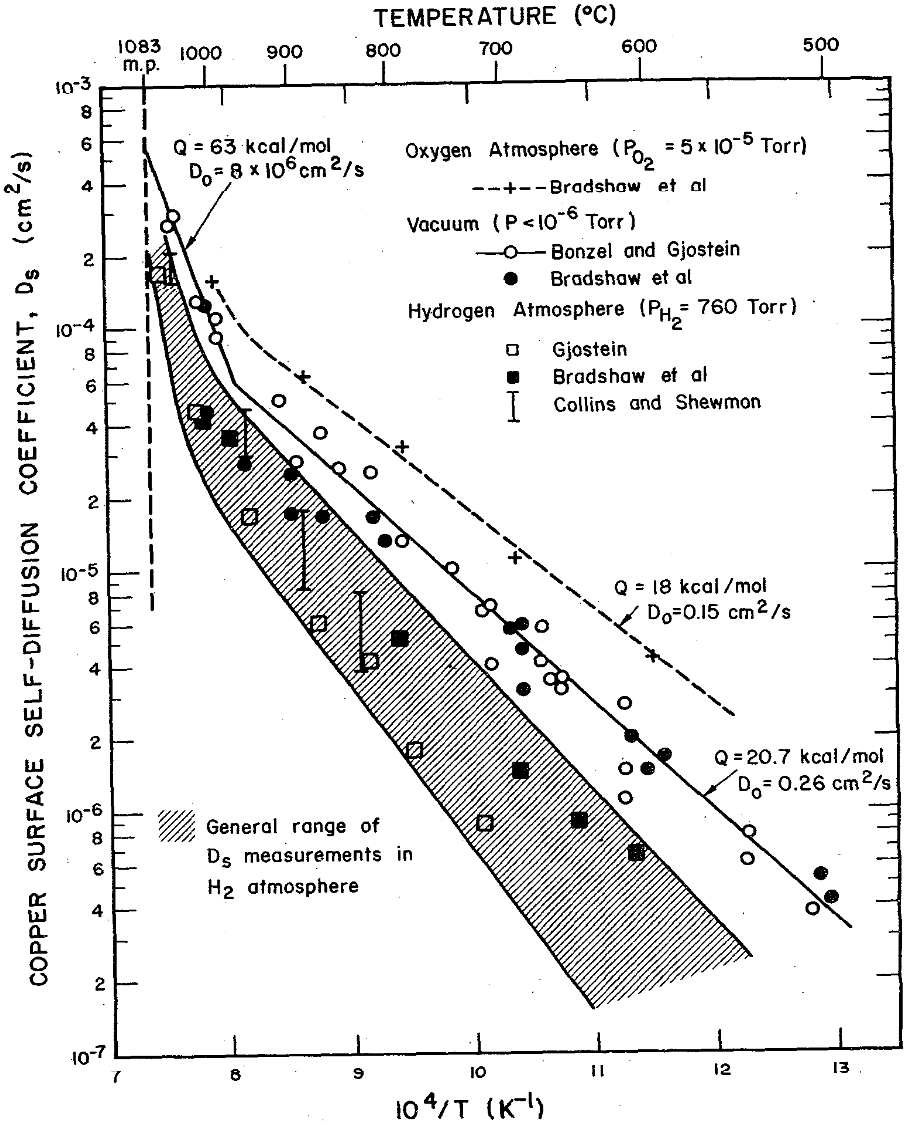

FIGURE 2. Surface diffusion of copper on copper.

Because of the scatter of the data, only a general range is indicated for surface diffusion in a hydrogen atmosphere and only selected examples of hydrogen-atmosphere data (which indicates typical trends over appreciable temperature ranges) are shown. The data of Collins and Shewmon are indicated as covering a range of values at each temperature since these results showed a significant dependence on crystallographic surface orientation. In the ranges displayed here, both the largest and smallest values measured by Collins and Shewmon at each temperature have been omitted. Since a D_0 value of 0.15 cm^2/s provides better agreement with the oxygen atmosphere data points of Bradshaw et al. than does their published value of 0.2 cm^2/s, the value 0.15 cm^2/s has been used in this figure.

cm^2/s at 1030 °C to 10^{-7} cm^2/s at 660 °C. By contrast, their oxygen atmosphere value of D_s at 660 °C is 5×10^{-6} cm^2/s. Below 660 °C, surface diffusion in a hydrogen atmosphere decreased drastically so that it could no longer be measured. The lower temperature measurements (below 800 °C) showed a strong dependence on the duration of the diffusion anneal. Bonzel and Gjostein suggest that an accumulation of impurities may be decreasing the measured D_s at the longer diffusion times and note that an extrapolation to zero diffusion time yields more consistent results. This correction also yields D_s values which lie within the hatched region in figure 2 rather than values an order of magnitude smaller. At temperatures below 910 °C, faceting was observed on the supposedly sinusoidal surface profiles. An apparent decrease in D_s by a factor of two was associated with the onset of faceting.

Bradshaw, Brandon, and Wheeler [38] relying mainly on grain boundary grooving experiments also studied the effect of various atmospheres on copper surface self-diffusion. The measured diffusion coefficients agree only roughly with those of Bonzel and Gjostein but do show a regular decrease as oxygen was removed and then hydrogen added in the atmosphere. Their Q values were all in the range from 17 to 22 kcal/mol. Their D_s values at 660 °C are listed in table 1. Although their hydrogen atmosphere Q values are slightly larger than their oxygen atmosphere and vacuum-pressure values, all are noticeably less than the 40 or 50 kcal/mol which other investigators have

TABLE 1. Surface self-diffusion parameters on copper (after Bradshaw et al.)

Atmosphere	Pressure (torr)	D_s(at 660 °C) (cm^2/s)
Hydrogen	760	1×10^{-6}
Hydrogen	$\sim5\times10^{-5}$	3×10^{-6}
Vacuum	$\sim1\times10^{-7}$	3×10^{-6}
Oxygen	5×10^{-5}	8×10^{-6}

found for copper surface diffusion in a hydrogen atmosphere.

Collins and Shewmon [39] found that in a hydrogen atmosphere introduction of H_2S would increase D_s for copper by a factor of 2 to 4. Their measurements, done by grain boundary grooving in the temperature range 830 to 1030 °C, included results for eight different crystallographic surface orientations. They found that changing the surface orientation typically could cause a factor of 2 difference in the measured D_s values. This orientation dependence is similar to that found earlier by Choi and Shewmon [40–42]. In the range 850–1060 °C, Choi and Shewmon measured D_s values for (111) surfaces which were a factor of 1.5 to 3 larger than those measured for (100) surfaces, with (110) measurements having an intermediate value. These measurements showed temperature dependences which would correspond to activation energies of around 40 to 50 kcal/mol, nearly the same as for self-diffusion. Such values are common for D_s measured in a hydrogen atmosphere.

Perraillon, Torrens, and Levy [43] in copper-64 tracer measurements of surface diffusion on copper between 520 to 600 °C found that diffusion occurred 1.5 to 2 times faster on (111) planes than on (100) planes and measured activation energies on these planes of $Q_{111}=38.3$ kcal/mol and $Q_{100}=27.9$ kcal/mol. A similar dependence of tracer activation energy and of D_s on the crystallographic orientation of the surface plane was also found by Borisov, Gal, and Gruzin at higher temperatures, 850 to 975 °C [44].

Hackerman and Simpson [45] used radioactive copper-64 tracer to study surface diffusion at 750 °C on copper in a hydrogen atmosphere and found that the rate depended not only on the plane exposed but also on diffusion direction. Their measured dependence on diffusion plane was almost the reverse of that found in other investigations reported above. Also, their measured diffusion anisotropy on (100) surface planes is surprising since, theoretically, diffusion on flat (100) surface planes should be isotropic because of the four-fold symmetry. Some lower temperature studies (450 and 600 °C) by Brandon and Bradshaw [46] on the smoothing of steps which were evaporated onto copper surfaces showed an appreciable change in apparent D_s values as the steps moved from one grain to another. In discussing their similar tracer measurements, Choi and Shewmon [42] suggested that vapor transport may have contributed greatly to Hackerman and Simpson's results. Possible effects of volume diffusion on thermal grooving experiments have been discussed by McAllister and Cutler [47].

Sizmann and co-workers[48, 49] measured the thermal smoothing of chemically etched periodic profiles on copper surfaces at 890 to 1015 °C in hydrogen atmospheres. They report that their results were probably appreciably affected by volume diffusion but for surface diffusion find an activation energy of 27 kcal/mol, about half that for volume diffusion. Bonzel and Gjostein [50] noted that a driving force which was too large by exactly a factor of two was introduced into the results reported in reference [48]. As a result, the diffusion coefficients quoted in that reference should be multiplied by a factor of two.

Other less-extensive measurements of copper surface self-diffusion by means of grain boundary grooving techniques have been reported by Mullins and Shewmon [51], Gjostein and Rhines [52], and Hough [53] and by means of healing of surface defects by Geguzin and Ovcharenko [54] and Menzel [55]. These results are generally within the experimental error of results reported above.

Rhead and coworkers [56–58] during surface diffusion introduced (as a vapor) small amounts of impurities, such as lead, which can form copper alloys or compounds having lower melting points than pure copper. This appreciably increased the measured D_s for copper, especially at temperatures above 900 °C. Values of D_s as high as 10^{-1} cm^2/s have been measured in such cases. These high values perhaps result from formation of a quasi-two-dimensional liquid at the surface or perhaps from other cooperative phenomena. (For discussions, see references 59–61.) A thorough review of this topic and of other possible impurity effects, which can either decrease or increase D_s, has been given by Bonzel [10].

Melmed et al. [62] employed field electron emission microscopy to study the rate of change of topographic features on copper field emission tips. The measurements were in a much lower temperature range (50–171 °C) than those reported above and yielded an activation energy for surface diffusion of 13 kcal/mol in this range. Warner [63] made somewhat similar field electron emission measurements but on larger samples than Melmed et al. and in the temperature range 700–1000 °C. Clum [64] suggests that the higher activation energies (25 to 50 kcal/mol) found by Warner can reasonably be attributed to impurity effects. Neumann and Hirschwald [65] emphasize that the diffusion mechanism and hence the measured Q_s values should be expected to depend on the temperature range.

Bowden and Balluffi [32] measured the annealing of voids which intersected a copper surface at temperatures between 254 and 408 °C. The results were in general agreement with an extrapolation of high temperature results obtained by other investigators in hydrogen atmospheres.

Nichols [66] evaluated D_s by studying the coalescence of two gas-filled bubbles in the interior of a copper specimen at 900 °C. His result of $D_s=1.4\times10^{-5}$ cm^2/s obtained by this method agrees well with measurements from grain-boundary grooving and scratch smoothing experiments.

5. Copper Sintering

Sintering of copper particles or wires has been studied and discussed by a large number of investigators [67–84],

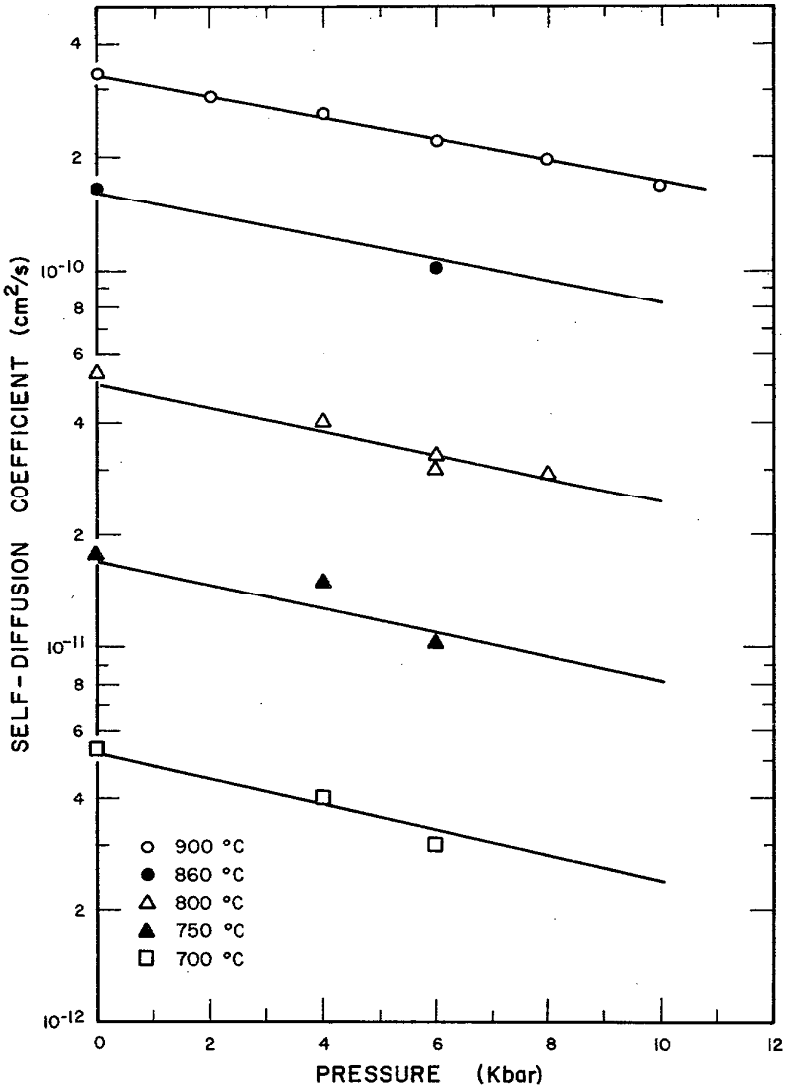

FIGURE 3. Dependence of copper volume diffusion in copper on temperature and hydrostatic pressure after Beyeler and Adda [13, 14].

usually being interpreted in terms of volume and surface diffusion processes. Accurate diffusion results are difficult to obtain by this method. Kuczynski [67] reported separate surface diffusion results for temperatures 400, 500, and 600 °C as did Kaufman, Whalen, and Sefton [69] at 700 °C. These D_s values in general were consistent with the hydrogen atmosphere results reported above. Beeré and Greenwood [70] from the sintering rate of pores located on grain boundaries in copper containing 1 wt. percent oxygen calculated an activation energy $Q=32\pm3$ kcal/mol in the temperature range 386 to 788 °C for the rate-controlling process, assumed to be copper grain boundary self-diffusion. With the grain boundary width taken as 5×10^{-8} cm, it was estimated that $D_o\approx2$ cm^2/s.

6. Electromigration

Electromigration measurements in pure copper by Kharkov and Kuzmenko [85, 86], Sullivan [87], Adda et al. [88] and Grimme [89] all show migration of copper ions toward the anode in the temperature range 800 to 1030 °C. This corresponds to a negative effective charge for the copper ions and indicates that the electron wind momentum transfer to the ions is more important than the direct effect of the field on the ion cores. Previous measurements by Wever [90] and Grone [91] indicated a reversal in marker direction measurement at temperatures above 950 or 1000 °C, but it now appears that this reversal does not really occur. Sullivan, from the relative motion of scratches on copper wire specimens, found an effective charge q^* of -5.5 ± 1.5 $|e|$, where e is the electronic charge. A similar result, $q^*=-8\pm3$ $|e|$, was measured by Grimme from the motion of surface microindentations on tubelike copper samples in the temperature range between 800 and 1030 °C. Kharkov and Kuzmenko, like Sullivan, made repeated measurements near 1000 °C but measured appreciably larger effective charges of $-14|e|$ to $-38|e|$. Their method involved weighing of specimen halves before and after diffusion. Adda et al. at temperatures of 820 to 860 °C measured movement of tungsten markers (foils and wires) and found effective charges of $-15|e|$ to $-26|e|$.

Hummel and Breitling [92, 93] found electromigration of copper ions in thin films of pure copper to be directed toward the cathode in contrast to the above bulk diffusion results. They attribute this cathode-directed migration as possibly being due to grain boundary diffusion.

7. Thermomigration

Measurements by Meechan and Lehman [94] yielded values of $Q^{**}=4\pm3$ kcal mol^{-1} for measured heats of transport in pure copper, as determined from marker motions in a temperature gradient of the order of 1200° K/cm in the temperature range 900 to 1000 °C. By contrast, Jaffe and Shewmon [95] found an opposite effect, with copper ions apparently moving from the cold to the hot end of their copper specimens in the range 750 to 1000 °C. Their Q^{**} value of -7 kcal mol^{-1} is somewhat doubtful since they also found a large change in dimension of their cooling block, which was at temperatures below 750 °C. Adda et al. [88] found no copper thermomigration effect in their experiments.

Mikhlin [96] investigated the migration of pores in a temperature gradient and interpreted the results as arising from atom diffusion along the surface of the pores.

8. Pressure Effects

Beyeler and Adda [13, 14] measured the effect of hydrostatic pressures up to 10 kbar on self-diffusion of copper-64 tracer in pure copper. They found that the measured diffusion coefficients in their temperature range of 700 to 900 °C (see figure 3) could be represented by

$$D=D_0 \exp-[(Q_0+P\,\Delta V)/RT],$$

with $D_0=0.18$ cm^2/s, $Q_0=46.9$ kcal/mol and $\Delta V=6.25$ cm^3/mol, where T is given in kelvin. Here ΔV is the experimentally measured activation volume. To obtain the "true" activation volume, related to the Gibbs free energy, a small correction must be made. Both activation volumes in this case equal approximately 9/10 of an atomic volume. Measurements by McArdle and Tomizuka [97, 98] also indicate that ΔV is less than one atomic volume. The value $D_0=0.18$ cm^2/s given here and used in figure 3 differs slightly from the rounded off value of $D_0=0.2$ cm^2/s published by Beyeler [14]. The value of 0.18 cm^2/s was selected as giving better agreement with the data.

The above values were calculated from experiments on single crystals of copper. Similar measurements on polycrystalline copper [14, 99] at 900 °C with pressures of 0 to 8 kbar gave essentially the same activation volume as in single crystals, as did measurements at 4 kbar and 800 °C. The only apparent difference was that the diffusion coefficients themselves were consistently 1 to 5 percent larger in the polycrystalline samples than in the single crystal samples.

9. Strain-Enhanced Diffusion

An effect from elastic strain at low temperatures was reported by Druyvesteyn and Berghout [100]. The electrical resistivity of a copper wire which had been quenched from high temperature was measured as a function of time at -30 °C. The rate at which the excess resistivity (presumably arising from quenched-in vacancies) was found to anneal out increased when the wire was loaded to 17 kg/mm^2. The change in annealing rate would correspond to a change of diffusion coefficient by a factor 1.7 if the annealing were due to diffusion of vacancies.

10. Nuclear Magnetic Resonance Measurements of Diffusion

El-Hannay and Zamir [101] from measurements of the nuclear relaxation times T_1 and T_2 in copper powder as a function of temperature (600 to 1000 °C) deduced values of $Q=1.97\pm0.04$ eV and $D_0=0.11\pm0.05$ cm^2/s for copper-63 and $Q=2.00\pm0.04$ eV and $D_0=0.15\pm0.07$ cm^2/s for copper-65. These activation energies and D_0 values are in reasonable agreement with tracer results reported by other investigators for volume diffusion. The activation energy results also are consistent with previous measurements by Flynn, Seymour, and Odle [102, 103]. These values, especially the D_0 values, cannot be expected to be as accurate as the tracer-sectioning results shown in figure 1. Nevertheless, when direct tracer results are not available, indirect measurements of diffusion by NMR methods may yield useful results.

11. Molten Copper

Self-diffusion coefficients of copper in molten copper have been measured by a capillary reservoir method in the temperature range 1140 to 1260 °C by Henderson and Yang [104]. A capillary which initially was filled with non-radioactive molten copper was immersed in a bath containing a uniform concentration of radioactive tracer copper-64 and after diffusion the radioactivity in the capillary was analyzed. The results could be represented by the equation

$$D=(1.46\pm0.01)\times10^{-3} \exp[-(9710\pm710)\text{ cal mol}^{-1}/RT]\text{ cm}^2/\text{s}.$$

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