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# Self-Diffusion in Cobalt*

FOSTER C. NIX AND FRANK E. JAUMOT, JR.
*Randal Morgan Laboratory of Physics, University of Pennsylvania, Philadelphia, Pennsylvania*

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The self-diffusion of cobalt has been measured using radioactive $Co^{60}$. The radioactive $Co^{60}$ was evaporated onto the surface of pure cobalt samples. The absorption coefficient in cobalt of the complex spectrum of the radioactive isotope was required in the mathematical analysis used. This was determined under conditions similar to those present in the diffusion samples. The data at 1050°C, 1150°C, and 1250°C, indicate that the self-diffusion coefficient for cobalt is given approximately by $D=0.37e^{-67000/RT}$ cm$^2$-sec$^{-1}$.

## I. INTRODUCTION

THE self-diffusion of metals is of great importance to both the physicist and the metallurgist. The physicist is concerned primarily with the mechanisms of the diffusion,[1] while the metallurgist[2] is primarily interested in the role which diffusion plays in such phenomena as recovery, recrystallization, creep, and sintering. Although much progress has been made in increasing our understanding of the mechanisms involved in diffusional phenomena, of which self-diffusion is the simplest, there still exists considerable doubt as to the relative role played by the presence of vacancies and interstitial atoms.[1] The experimental evidence to date does not lend support to the older concept of atomic interchange between neighboring atoms.

The present research dealing with the self-diffusion of cobalt was undertaken in order to obtain additional accurate experimental data with the hope of testing recent theories of metallic diffusion.

## II. DESCRIPTION AND DISCUSSION OF PRESENT INVESTIGATION

Radioactive $Co^{60}$, which may be obtained from the Atomic Energy Commission[3] in the form of metallic wire, emits two gamma-spectra, one with an energy of 1.30 Mev, the other with an energy of 1.16 Mev, and a beta-spectrum of energy 0.31 Mev. The isotope has a half-life of 5.3 yr, which made it unnecessary to compare each measurement with a standard to allow for radioactive decay, since the time between counting any set of samples before and after diffusion did not exceed three days.

The radioactive cobalt was evaporated from a tungsten filament onto square samples of pure cobalt metal, $\frac{5}{8}'' \times \frac{5}{8}'' \times \frac{1}{8}''$, which had received a careful metallographical polish. The cobalt used for the samples was obtained in two purities, 99.06 percent cobalt in rondel form from African Metals Company, New York, New York, and 99.7 percent electrolytic cobalt in nodular form from Johnson-Matthey Company, England. The cobalt was melted in a hydrogen atmosphere in an induction furnace, cooled, and remelted with intermittent hydrogen flushing during melting, held at a temperature above the melting point for more than one hour in a vacuum to remove the majority of the adsorbed hydrogen, then cooled in a vacuum. After melting, both purity metals were of x-ray density within the limits of our measurements. No difference in the diffusion rates was obtained for the two different purities of cobalt. The evaporated radioactive layers were less than 0.05 micron in thickness and did not affect the appearance of the mirror surface. These layers were considered to be infinitely thin for calculational purposes.

The surface activity of the coated samples was determined by means of a standard commercial thin mica end window counter tube in conjunction with a scale of sixty-four counting circuit. The samples were placed in a specially built collimating device constructed of lead with an interchangeable base. The base had a socket into which the sample was a "slip fit." The collimating device fitted snugly into a standard counter tube holder. This arrangement allowed the geometry to be reproducible to within 0.005″ in either direction, and the collimation reduced any edge effect to a minimum. The samples before diffusion displayed an activity of 7000 to 20,000 counts/min above background.

Two samples of nearly the same surface activity were placed with active faces together in a two piece Lavite "boat type" sample holder, and this placed in a refractory tube furnace, heated by a tubular Globar heating element. During the diffusion process the furnace was evacuated to a pressure of less than $10^{-5}$ mm Hg. The furnace temperature was controlled by a standard Leeds and Northrup two-point controller-recorder with both points being used in order to reduce the control time. The controllers operated on platinum, platinum-rhodium thermocouples placed in contact with the Lavite sample holder. Uncertainties in the temperature did not exceed 0.5 percent in most cases although they were as high as 2 percent in isolated cases. A certain error is introduced by the time taken to heat the samples and to cool them after diffusion, but this was minimized as far as the cooling was involved by the water-cooled

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* This work was supported by the ONR.

[1] F. Seitz, Acta Crys. 3, 355 (1950).

[2] C. E. Birchenall and R. F. Mehl, Inst. Metals Div. 188, 144 (1950).

[3] U. S. Atomic Energy Commission, Isotopes Branch: Catalog and Price List No. 3 (July, 1949).

ends on the Globar element, and by an arrangement which allowed air to be forced past the furnace tube as well as the outside of the furnace using an ordinary blower fan. In no case did it take more than five minutes to reduce the temperature to 1000°C, or more than ten minutes to reduce the temperature to 800°C, below which diffusion proceeds very slowly. However, the error introduced by the time taken to bring the samples to the desired temperatures must be corrected for and this error is difficult to calculate exactly, although it is estimated not to exceed 1 percent.

After diffusion the activities of the samples were again determined, the counts now falling in the range 4000 to 17,000 counts/min above background.

Inasmuch as the samples were placed in the furnace in pairs to reduce the error due to evaporation from the surfaces, all calculations were based on the counts from a pair of samples, rather than from a single sample.

## III. THEORY AND MEASUREMENT OF THE ABSORPTION COEFFICIENT

It has been shown by Steigman, Shockley, and Nix[4] that the diffusion constant, $D$, and the absorption coefficient, $\mu$, can be related to the fraction, $F$, of the count remaining after diffusion, to a very good approximation by

$$F = e^z[1 - P(\sqrt{z})], \tag{1}$$

where

$$P(\sqrt{z}) = (2/\pi)\int_0^{\sqrt{z}} \exp(-y^2)dy, \tag{2}$$

$$z = \mu^2 Dt. \tag{3}$$

The use of these equations assumes the sample to be thick compared with the depth of penetration of the diffusing atoms, which is certainly valid in the present investigation. Also, the use of expressions (1) and (3) requires that the measured activity decrease exponentially with absorber thickness to the depth of penetration of the diffusing atoms, or at least to the depth where contributions to the measured activity after diffusion will be small. This latter requirement of Eqs. (1) and (3) of course necessitates a very careful measurement of the absorption coefficient for very thin absorber thicknesses in the case of an isotope such as $\mathrm{Co}^{60}$ which has the three radiation spectra mentioned above. In this case it is not sufficient to employ the standard technique of using thin foils to measure this coefficient and then extrapolating to less thick materials since the logarithmic plot of $\mu$ against thickness is not a straight line from zero thickness to the thickness of the foils which we were able to obtain. Under similar circumstances Birchenall and Mehl[2] measured the absorption coefficient for aluminum, for which the mass coefficient for beta-rays is nearly the same as for iron, the metal under consideration. The contribution for x-rays was calculated and an effective absorption coefficient obtained. In the present experiment a direct determination of the absorption coefficient was made. This was accomplished by electroplating[5] radioactive cobalt onto a small area of a sample similar to the ones used for diffusion, electroplating successive layers of pure cobalt onto this, and then determining $\mu$ directly. Eighteen determinations were carried out, showing remarkable consistency. As a check on the method, cobalt was eventually plated to a thickness somewhat greater than the thinnest uniform cobalt foil which we were able to obtain. Although the absorption did not decrease exponentially to this thickness, 0.001″, the curve obtained from the electroplated cobalt samples agreed with the curve obtained by using the foil to within 3 percent, after corrections for the difference in initial activity were made.

Since there are many sources of error in a determination of the absorption coefficient great accuracy cannot be claimed for the value. The value for $\mu^2$ obtained by averaging the 18 values from the individual samples is probably no more than 10 percent in error and certainly within 15 percent.

The absorption curves obtained using this method were found to satisfy the condition imposed by Eqs. (1) and (3) to the depth of penetration of the diffusing atoms. Four typical curves obtained from samples of different initial activity are plotted in Fig. 1.

## IV. RESULTS

Diffusion "runs" were carried out at three temperatures, 1050°C, 1150°C, and 1250°C for 18 hours. The diffusion constants, $D$, given in Table I were obtained by averaging the fractions, $F$, of all samples at a given temperature which did not show oxidation, reading $z$ from a plot of $F$ *vs* ln$z$ from Eq. (1), and calculating $D$ from Eq. (3).

Table II gives $A$, the activation constant, and $Q$, the

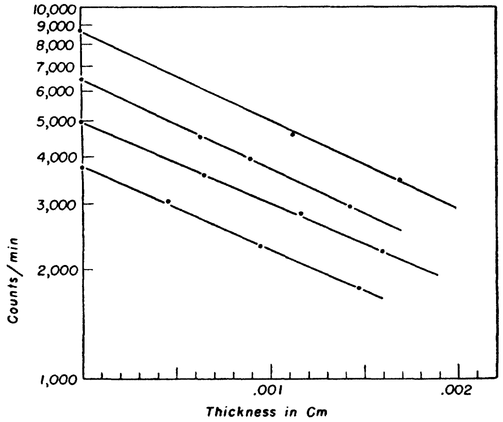

Fig. 1. Typical plots of counts per minute *versus* thickness of cobalt absorbing layer.

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[4] Steigman, Shockley, and Nix, Phys. Rev. **56**, 13 (1939).

[5] Soderberg, Pinner, and Baker, *Modern Electroplating* (Journal of Electrochemical Society, 1942), pp. 145 ff.

TABLE I. Values of self-diffusion coefficient, $D$, for cobalt obtained using directly measured values of the absorption coefficient.

| Temperature (deg. C) | $\mu^2$ (cm$^{-2}$) | $D$ (cm$^2$—sec$^{-1}$) |
|---|---|---|
| 1050 | $2.68\times10^5$ | $3.22\times10^{-12}$ |
| 1150 | $2.68\times10^5$ | $1.78\times10^{-11}$ |
| 1250 | $2.68\times10^5$ | $9.18\times10^{-11}$ |

activation energy, as obtained from a plot of $\ln D$ against $1/T$, shown in Fig. 2. $D$, $A$, and $Q$ are related by

$$D=Ae^{-Q/RT}. \tag{4}$$

The data lead to the self-diffusion constant for cobalt being represented approximately by

$$D=0.37e^{-67000/RT}\text{ cm}^2\text{ sec}^{-1}. \tag{5}$$

Table II also gives values for $A$ and $Q$ as obtained from the Langmuir-Dushman equation relating $D$ and $Q$,

$$D=(Q/Nh)\delta^2e^{-Q/RT}, \tag{6}$$

where $N$ is $6.06\times10^{23}$ mole$^{-1}$, $h$ is Planck's constant, and $\delta$ is the lattice constant for the face-centered cubic lattice, which is the stable phase at the diffusion temperatures.

## V. DISCUSSION OF RESULTS

First, it should be noted that the agreement of the $Q$-value obtained from the Langmuir-Dushman equation with that found experimentally is probably fortuitous. It has been pointed out[6] that in the determination of $Q$ by the Langmuir-Dushman equation the calculation is very insensitive to a change in the lattice constant, $\delta$. More careful considerations of the mechanisms involved indicate the constant $A$ should be of the order of $\delta^2\nu$, where $\nu$ is a lattice vibrational frequency not in general[7] equal to $Q/Nh$. Unfortunately, we know of no existing theoretical values of $Q$ and $A$ for comparison with our experimental data permitting us to differentiate between the various proposed mechanisms of diffusion.

TABLE II. Summary of data on self-diffusion in cobalt.

| $A$ (cm$^2$-sec$^{-1}$) | $Q$ (kcal-mole$^{-1}$) | $T_m$ Melting point (°K) | $E$[a] Binding energy (kcal-mole$^{-1}$) | $Q/T_m$ $\times10^3$ | $Q/E$ |
|---|---|---|---|---|---|
| 0.37[b] | 67[b] | 1768 | 100.4 | 38 | 0.67 |
| 0.93[c] | 69.6[c] | 1768 | 100.4 | 39 | 0.69 |

[a] E computed from relations given in S. Dushman, *Vacuum Technique* (John Wiley and Sons, Inc., New York, 1949), p. 742.
[b] Determined from plot of $\ln D$ *vs* $1/T$ °K.
[c] Determined from Langmuir-Dushman equation.

We have included in Table II the values of $Q/T_m$ and $Q/E$, where $T_m$ is the melting point in degrees Kelvin and $E$ is the binding energy. The binding energy of a metal and its melting point are measures of the energy required to destroy the lattice, and since diffusion involves the escape of atoms from their proper lattice sites, the energy of activation should also be related to this energy. The values of $Q/T_m$ and $Q/E$ are approximately constant for most metals and the values we obtained for these ratios agree well with those given for other metals.[6] Owing to the uncertainty in the experimental values of $Q$, to date,† it has not been possible to say whether $Q$ is more closely related[4,6] to $E$ or $T_m$.

The errors in diffusion work are somewhat difficult to estimate with accuracy. As mentioned, the largest error is probably in the determination of $\mu^2$, and is probably of the order of 10 to 15 percent. The error in the counting, including the statistical error, and the geometric effects, probably aggregate to 2 to 3 percent, and the error in the temperature and control to no more than 2 percent. Errors in the measurement of time are negligible. Thus the average uncertainty may be of the order of 15 percent for single points, but the error in the curve of $\ln D$ *vs* $1/T$ should be much less than this.

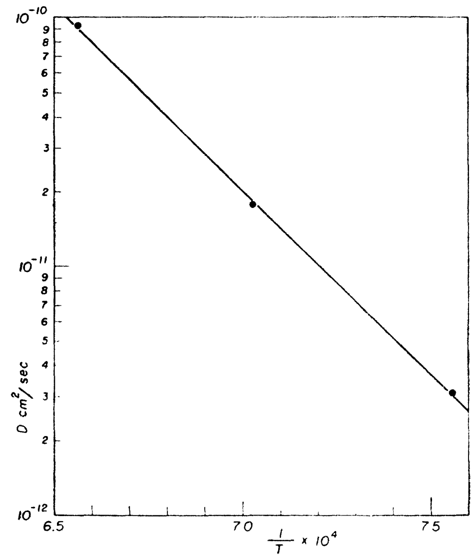

FIG. 2. Values of $D$ *versus* $1/T$ °K.

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[6] A. B. LeClaire, *Progress of Metals Physics* (Butterworth's Scientific Publications, London, 1949).
[7] J. Bardeen, private communication.

† Since the writing of this article, G. J. Dienes [J. Appl. Phys. 21, 1189 (1950)] has given an interesting empirical correlation between the activation constant $A$, which he calls the frequency factor, and the quantity $Q/T_m$. Dienes finds a correlation between these quantities by plotting $\log_{10}A/\nu\lambda^2$ *vs* $Q/2.303RT_m$, where $\lambda$ is the interatomic distance and $\nu$ is the Debye frequency. Our data seem to lend support to the suggested correlation when plotted on Fig. 1 of Dienes' paper. Furthermore, a reasonable agreement with experiment, i.e., within an order of magnitude, is given for $A$ when this quantity is computed from Eq. (2) of that paper.