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The Self-Diffusion of Copper*

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The self-diffusion of copper has been measured with a radioactive isotope prepared by neutron bombardment of zinc. The isotope is electroplated in a thin layer upon the surface of a copper disk. By measuring the decrease in β-ray emission from the sample due to the penetration of the radioactive copper, the self-diffusion constant is determined within the limits of accuracy as 11 cm^2/sec. exp$(-57{,}200/RT)$. Methods of analyzing such data are given and the significance of the variation of activation energy between self-diffusion and heterogeneous diffusion is discussed.

PART I

DIFFUSION is a process of fundamental significance in practical and theoretical metallurgy.[1] There are, however, no quantitative theories for diffusion and there is even some question as to the exact qualitative nature of the diffusion in metals. Three mechanisms are regarded as being possible: atomic interchange occurs between neighboring atoms; some atoms occupy interstitial positions and diffuse by moving from one such position to another; "holes" or vacant lattice sites exist and diffusion results from atoms moving from site to site through the medium of the holes.

The simplest type of diffusion is self-diffusion. In the strict sense of the term self-diffusion implies diffusion of something into its exact counterpart; however, used more loosely it implies diffusion of one isotope into another isotope of the same chemical element. The earliest experiments in self-diffusion in metals were performed by von Hevesy and his collaborators[2–4] using ordinary lead into which was diffused thorium B which is a radioactive isotope of lead. By analyzing the distribution of the radioactive isotope in the lead, they were able to determine the rate of self-diffusion. Now that artificial radioactive isotopes are available it is possible to investigate many additional cases of self-diffusion.

The present paper is concerned with the self-diffusion of copper. An indirect method of determining the rate of diffusion has been used, the procedure being as follows: upon a copper disk is electroplated a very thin layer of radioactive copper and the radioactivity is measured with a Geiger-Müller counter. The disk is then heated in vacuum in such a manner as to cause diffusion to take place without appreciable loss from evaporation. The penetration of the radioactive atoms below the surface of the disk results in an absorption in the disk of their radioactive radiation and thereby produces a decrease in radioactivity as observed by the Geiger-Müller counter.

After the stopping power of copper for the radioactive radiation is determined, it is possible to use the observed activities in order to determine the depth of diffusion of the active isotope and hence to measure the rate of diffusion. Part II of this paper gives the methods of producing and concentrating the radioactive isotope and of measuring the activities and stopping power of copper. Part III describes the technique used in the diffusion process and Part IV presents the theoretical analysis and the results.

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[1] R. F. Mehl, J. App. Phys. **8**, 174 (1937).

[2] J. Groh and G. v. Hevesy, Ann. d. Physik **63**, 85 (1920).

[3] G. v. Hevesy and A. Obrutscheva, Nature **115**, 674 (1925).

[4] G. v. Hevesy and W. Seith, Zeits. f. Physik **56**, 790 (1929).

PART II

Radioactive copper (Cu^{64}—period 12.8 hours) was prepared from zinc (Zn^{64}) by neutron bombardment with a radon-beryllium source of neutrons varying in strength from 300 to 600 mc. Ninety grams of zinc (C. P. Eimer & Amend product) was irradiated for about 13 hours and then treated with concentrated hydrochloric acid so as to dissolve all but several hundred milligrams, which were found to retain practically all the activity. This small residue was then dissolved in hydrochloric acid; 30 cc of concentrated sulphuric acid was added; and the mixture evaporated until fumes of SO_3 were given off. The resultant solution was next diluted to 400 cc and filtered. The radioactive copper was electroplated from the filtrate upon a rapidly rotating disk cathode of copper, of 3 cm diameter and 0.5 mm thickness.[5] The operating current was 11–12 milliamperes, the voltage 2.0–2.2 volts, the speed of rotation 4500 r.p.m. and the period of electrolysis 30–45 minutes.

The copper disks which were used were rolled from bars of spectroscopically pure copper which was obtained from Adam Hilger & Company, London (referred to as "Hilger" copper). In addition, so-called "Chile" copper of lesser purity was also used. It was found that the very small traces of radioactive copper could not be successfully plated on "Hilger" copper no matter how clean the surface. Even when the latter had received a careful metallographical polish, very little radio-copper would deposit. Finally, it was found that buffing the surface of such a disk with rouge on a rapidly rotating cloth wheel produced a surface upon which radioactive copper would deposit satisfactorily. The plating was facilitated by adding to the plating bath a drop of "reagent" copper sulphate solution (about $0.1N$) to act as a carrier. The radioactive copper was more readily plated upon the "Chile" copper and ordinary sheet copper than upon Hilger copper, presumably because of small amounts of impurities in them. It is possible that the buffing operation added minute amounts of impurity or produced strains in the metal which would have the virtual effect of metallic impurities.

Spectrochemical analyses were made of a large number of the disks. In some cases traces of Zn (less than 0.01 percent) were found and in other cases no detectable amount was present. There was no apparent correlation between the finding of zinc and the degree of diffusion. Traces of Sn, Pb, Mg, Si, Al and Fe were found in all analyses.

After the disk was plated with radio-copper, it was cut into four equal segments, each one marked in a characteristic manner. The activities of the segments were then measured, either individually or collectively, in a special holder which fitted around a thin silver-walled Geiger-Müller tube. This holder was constructed so as to have positions for holding four quadrants evenly spaced in definite positions about the counting tube. It was found that successive measurements of the activity of a copper segment placed in the same position in the holder several times did not differ from each other by more than one percent. This arrangement permitted (1) accurate measurement of any single quadrant, and (2) the simultaneous measurement of four quadrants—a feature of value at the end of a long run when the activity of any one sample was too near to the background value for any precise determination.

The radioactivity was measured by means of a thin-walled glass counter, whose cathode was of chemically deposited silver (now made by Eck & Krebs, New York). Such counters have a high sensitivity (ratio of count surrounded with KCl to background count about 40 to 1), and a record of constant performance over a period of several years. The counter was connected to a modified Neher-Harper circuit,[6] and a thyratron de-multiplying recorder system.

The background of this counter was about 17 counts per minute. In general, a sufficient number of counts per minute per sample were taken so that the precision was of the order of magnitude of three percent to 1.5 percent (i.e., 1000 to 4000 counts in all were taken for any one reading). The initial activities ranged from 800 counts per minute to 100 counts per minute. The final activities ranged from 15 counts per minute above background to several hundred counts per minute per quadrant above back-

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[5] J. Steigman, Phys. Rev. **53**, 771 (1938).

[6] H. V. Neher and W. W. Harper, Phys. Rev. **49**, 940 (1936).

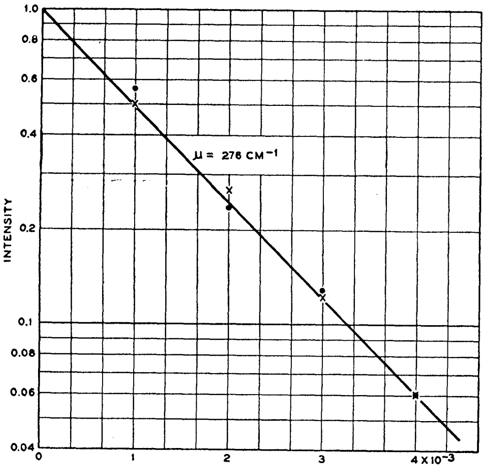

FIG. 1. Variation of transmitted activity as a function of the thickness of the interposed copper.

ground. In order to eliminate the effects of possible fluctuations in the counting rate, a radioactive disk, prepared at the same time as the disks used for the diffusion, was set aside as a control standard. During any particular diffusion run, the activity of this disk was measured immediately before or after the sample was measured, and in only one case did the activity of the control disk vary markedly beyond the estimated precision from the activity calculated on the basis of a 12.8-hour period.

The effective absorption coefficient of copper for the beta-rays from radio-copper was determined by placing a disk upon whose surface radio-copper had been plated in a horizontal position below the Geiger-counter, and measuring the transmitted intensity with various thickness of copper foil interposed between the disk and the counter. Plots of the log of the activity against thickness of the foil yielded a straight line. A line with the same slope was obtained for a thin activated foil of copper which was wrapped around the counter tube with various thicknesses of inactive foil interposed. The results are shown in Fig. 1. The transmission is decreased approximately by a factor of $\frac{1}{2}$ for each mil of copper interposed between the disk and the counter and the corresponding value of the absorption coefficient μ is 276 cm^{-1}.

The effect of diffusion is determined by measuring the activity of the material before diffusion and after diffusion. In interpreting the results it is necessary to know what part of the decrease in activity is due to diffusion and what part to the ordinary decay. Since the period of decay is known to be 12.8 hours the effect of time decay can be eliminated by multiplying the second measurement by $\exp(t/12.8)$ where t is the time in hours between measurements. The remaining decrease is due to diffusion and is expressed by stating the fraction, F, of the original activity which is observed after diffusion. The values of F found for runs of various times and temperatures are shown in Figs. 4, 5 and 6.

PART III

In order to obtain measurable amounts of diffusion, it was necessary to maintain the activated quadrants of the disks at elevated temperatures for known times. The quadrants were placed in a special copper holder constructed in a manner permitting the active or plated surfaces of the quadrants to be firmly held between the two halves of the holder with the radioactive surface of one quadrant opposite that of another. This relatively large copper holder also served to maintain the several quadrants at the same temperature. The placing of the quadrants in the "face-to-face" position tended to reduce the net loss of radioactive copper atoms in that atoms evaporating from one quadrant would tend to deposit on the opposite one. As is shown in the appendix, the transfer of radioactive material from the face of one quadrant to the other has no effect on the value of F provided that one deals with the sum of activities of the two quadrants rather than with each individually. However, any net loss from the two quadrants would be a source of error and for this reason checks were run at various times to determine the amount of activity lost by evaporation to the holder and other parts of the apparatus. The activity found in the other parts was always within the experimental error.

The holder with copper disks was then placed in a fused quartz tube and evacuated to a pressure of less than 10^{-4} mm of Hg. In some instances the quartz tube was sealed off while in others the tube was pumped continuously throughout the diffusion experiment. We were unable to detect any

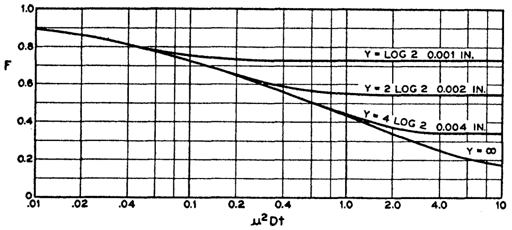

FIG. 2. Apparent activity from plated face *versus* $z=\mu^2 Dt$.

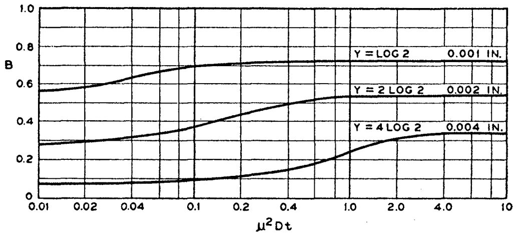

FIG. 3. Apparent activity from back face *versus* $z=\mu^2 Dt$.

difference in the diffusion rates between the runs carried out in the two kinds of tubes, i.e., between tubes sealed off after evacuation and continuously pumped tubes. The temperature was measured by means of platinum-platinum ten percent rhodium thermocouples. In the case of the continuously pumped tubes the protected hot-junction was placed in a hole in the copper holder. This permitted us to obtain accurate measurements of the temperature in the immediate vicinity of the diffusion specimens. In the case of the sealed-off quartz tube the thermocouple junction was placed on the outside of the tube near the place occupied by the copper holder. In the latter method, with the sealed off tubes, checks showed the temperature of the specimen to be accurate to within ±2°C. Corrections were made to offset the lag in heating of the holder with specimens in the sealed off tubes. The temperature of the furnace was maintained constant either by means of a voltage regulator or a potentiometric temperature controller. The temperature was held constant to within ±2°C. On completion of a run the quartz tube was immersed in a bath of cold water in order to terminate the diffusion run at the desired time. Examination of the copper disks after the diffusion runs showed them to be clean and completely free of any oxide film. Runs were made at three temperatures, 750°, 850° and 950°C and the results are shown in Figs. 4, 5 and 6. In some cases the points shown represent the average for all four quadrants. In other cases, two points are shown connected by a line; in these, each point corresponds to a pair of quadrants facing each other. It is seen that the spread between different runs is in general larger than the spread in an individual run. At present we have no satisfactory explanation for the large spread. Tests have been made using two quadrants from one disk in one run and the remaining two quadrants in a different run; also tests have been made using both the Hilger and Chile copper; these show that there is no consistency between the type of disk and the variations of the final results. There is no apparent correlation with the grain size obtained after diffusion as determined by microscopic examination. Some preliminary experiments with tubes containing hydrogen gas suggest that there may be an important correlation between the atmosphere and the diffusion and we hope to experiment further on this effect in the future.

PART IV

According to the considerations presented in the last section, which are justified in the Appendix, the effects of evaporation from one quadrant to the other can be disregarded if the total activity of the two quadrants is dealt with. For this reason we may consider a single quadrant. Let us suppose that the quadrant is of thickness w, that the absorption coefficient is μ, and that the radioactive material which was initially on the surface of the quadrant has diffused for a time t, the diffusion constant being D. By the use of standard mathematical methods one can find, as is shown in the Appendix, how the fraction of the activity F depends upon these quantities. One finds that F is a function of two variables, z and y where

$$z=\mu^2 Dt \qquad (1)$$

and

$$y=\mu w. \qquad (2)$$

In Fig. 2 we give the results of these calculations, each curve corresponding to a fixed thickness or y value.

It is possible to carry out an exactly similar procedure for the case where the measurement of the activity is made from the back of the quadrant. In this case we denote by B the fraction of the initial activity as measured from the plated side which is later observed from the back side. In Fig. 3 are given a series of curves like those in Fig. 2.

For the conditions of our experiments the disks are thick in the sense that very little radiation can get through them and furthermore, the depth of diffusion is small compared to the thickness—mathematically $y>10$ and $y^2>3z$. Under these conditions F is well approximated by

$$F(z, y)=F(z, \infty)=e^z[1-P(\sqrt{z})], \tag{3}$$

where

$$P(\sqrt{z})=\frac{2}{\sqrt{\pi}}\int_0^{\sqrt{z}} e^{-y^2}dy \tag{4}$$

is the error integral. From a measurement of F we can use our curve to determine z, and then using the known time of diffusion and the value for μ we can calculate D from Eq. (1). A more satisfactory procedure, and the one used, is as follows: at a given temperature D is a constant, hence a plot of F *vs.* z on a logarithmic scale should be the same as a plot of F *vs.* t displaced by log $(\mu^2 D)$. Figs. 4, 5 and 6 show measured values of F vs. t. On each plot we give three theoretical curves displaced by various amounts corresponding to three values of D. The solid curves represent the best values of D and the dashed curves the estimated bounds of experimental error.

The best value of D and the experimental uncertainty for each temperature is shown in Fig. 7 plotted on a logarithmic scale against the reciprocal of the absolute temperature. The measured values fall along a reasonably straight line indicating that D is given by an expression of the form

$$D=A\exp(-Q/RT). \tag{5}$$

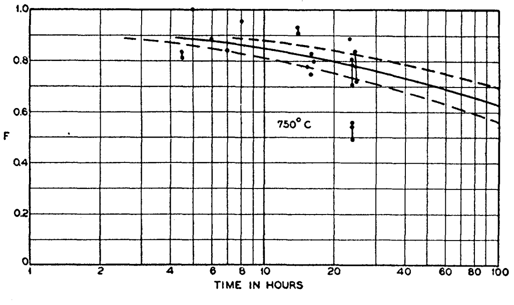

FIG. 4. Apparent activity *versus* time of heating at 750°C.

The values of A and Q for the straight line of Fig. 7 are given in the first row of Table I. A similar analysis of the data of Rollin gives the values in the third row.

Using some simplifying assumptions Langmuir and Dushman[7] have obtained a theoretical equation for D which relates A and Q:

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

where $N=6.06\times10^{23}$, h is Planck's constant and δ is the lattice constant. Fitting this equation to the value of D at 950°C we get the values for A and Q in the second row of Table I.

For comparison, on Fig. 7 we have shown values for the diffusion of small concentrations of other metals into Cu. These curves were obtained by Rhines and Mehl[8] who measured the rates of diffusion for various compositions and extrapolated their results to zero concentration. Since these curves are so nearly alike, Rhines and

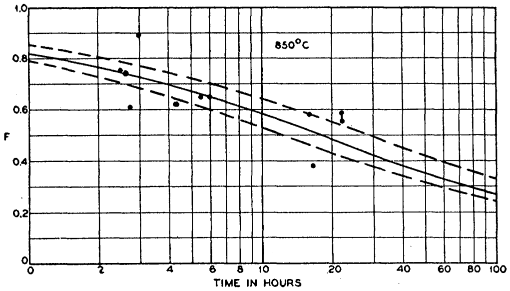

FIG. 5. Apparent activity *versus* time of heating at 850°C.

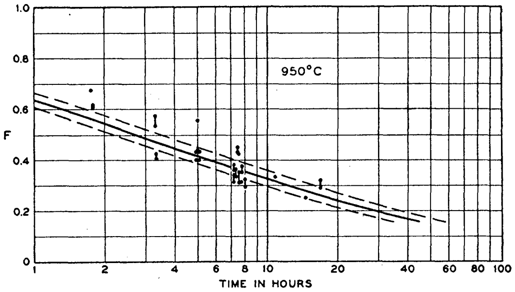

FIG. 6. Apparent activity *versus* time of heating at 950°C.

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[7] S. Dushman and I. Langmuir, Phys. Rev. **20**, 113 (1922).

[8] F. R. Rhines and R. F. Mehl, Trans. A. I. M. M. E. **128**, 185 (1938).

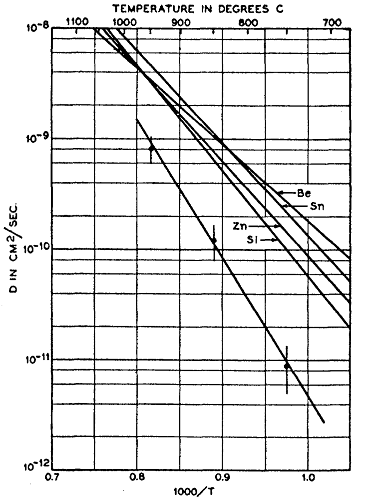

FIG. 7. Values of D *versus* $1/T°\mathrm{K}$.

Mehl suggested that they represented something typical of copper alone and therefore the self-diffusion constant of copper. From our work we find that the self diffusion constant is smaller than the diffusion constants of the various solutes and as will be illustrated later this seems to be generally true.

In Table I we have assembled the data at present available for self-diffusion. Since diffusion involves the escape of atoms from their proper lattice sites, the energy of activation should be related to the energy required to destroy the lattice. Both the binding energy of the metal and its melting point are measures of this energy. For Cu, Au and Pb we see that Q stands in a nearly constant relationship with both these quantities and the present uncertainty in the experimental data makes it impossible to say to which Q is more closely related. Since Bi is a rhombohedral crystal, the diffusion equations involve two values for D, one parallel and one perpendicular to the C axis. The extremely large values of Q and A for the perpendicular direction are very difficult to understand. For almost any theory of diffusion, except that of Bernal[9] which involves a sequence of displacements along slip planes, the constant A should involve the product of a frequency of atomic vibration ν times the square of the lattice constant or the distance between nearest neighboring atoms δ. For Cu, ν and δ give a value for A of ~ 1 cm²/sec.; for other elements these quantities may change by a factor of two or three producing at most changes in A of about one order of magnitude. However, a value such as 10^{46} cannot conceivably be explained in this way.

The values of Q for the self-diffusion of Cu, Ag and Pd are not inconsistent with any information now available about the three processes of diffusion usually considered; that is (1) interchange of position between pairs or groups of atoms (2) interstitial diffusion (3) diffusion by vacant lattice sites or holes. Owing to the relative incompressibility of atoms it is hard to see how they can find room to interchange positions or to become interstitial. Process (3) which does not involve the compressing of atoms but rather the creation of vacant sites seems therefore the most sound from an energetic point of view. According to this theory the diffusion constant is given by the equation

$$D = \nu\delta^2 e^{-J/RT} f, \tag{7}$$

where f is the fraction of sites which are vacant and J is the activation energy for a transition to a vacant site. If the energy required to produce a hole is H, then $f = \exp(-H/RT)$ and the activation energy for D is $H+J$. Now it is reasonable to suppose that the energy H is of the order of magnitude of the binding energy and that J is considerably smaller. (This is the case for the chemically different system Ag Cl for which the constants involved in the hole diffusion of Ag

TABLE I. *Summary of data at present available for self-diffusion.*

METAL	A CM²/SEC.	Q KCAL./MOLE	Tm MELTING POINT °K	E BINDING ENERGY KCAL./MOLE	$\frac{Q}{Tm}$	$\frac{Q}{E}$	REFERENCE
Cu	11	57.2	1356	81.2	42	0.70	α
“	0.9	51.0	“	“	38	.63	β, 8
“	47	61.4	“	“	45	.76	α, 17
Au	2.1	51	1336	92	38	.55	α, 19
“	410	62.9	“	“	47	.68	α, 18
Pb	6.66	28.05	600	47.5	47	.59	α, 12
Bi ‖c	10^{-3}	31	544	47.8	57	.65	α, 20
⊥c	2.4×10^{46}	140	“	“	257	2.92	α, 20

α. A and Q determined from plot of log D *vs.* $1/T°\mathrm{K}$.
β. A and Q determined from Langmuir-Dushman equation.

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[9] J. D. Bernal, Trans. Faraday Soc. **34**, 834 (1938).

TABLE II. *Values of Q and of A for various metallic solutions.*

SOLVENT	GROUP	SOLUTE	GROUP	A CM²/SEC.	Q KCAL./MOLE	ATOM DIAM. SOLUTE / ATOM DIAM. SOLVENT	MELTING POINT SOLUTE °C	REFERENCE
Cu	*IB*	Cu	*IB*	11	57	1.00	1083	α
		Sn	*IVB*	0.14	45	1.21 (1.24)	231	β, 8
		Si	*IVB*	0.006	40	0.90 (1.05)	1420	
		Zn	*IIB*	0.003	38	1.08	419	
		Al	*IIIA*	0.003	38	1.10	660.2	
		Be	*IIA*	5×10^{-5}	28	0.88	1350	
Ag	*IB*	Au	*IB*	9.60	26.6	1.00	1063	α, 11
		Cu	*IB*	5.13	24.8	0.89	1083	
		In	*IIIB*	6.30	24.4	1.09	155	
		Cd	*IIB*	4.18	22.35	1.06	320.9	
		Sb	*VB*	4.58	21.7	1.12	630	
		Sn	*IVB*	6.75	21.4	1.13	231	
Pb	*IVB*	Pb	*IVB*	6.66	28.05	1.00	327.5	α, 12
		Ni	*VIIIA*	0.67	25.3	0.71	1425	γ, 13
		Sn	*IVB*	0.66	25	0.91	231	γ, 14
		In	*IIIB*	0.61	23.2	0.90	155	γ, 16
		Tl	*IIIB*	0.58	22	0.98	303.5	γ, 14
		Bi	*VB*	0.58	22	1.04	271	γ, 14
		Hg	*IIB*	0.51	19.5	0.89	−38.87	γ, 16
		Mg	*IIA*	0.49	18.7	0.92	651	γ, 16
		Ag	*IB*	0.41	15.7	0.82	960.5	γ, 14
		Au	*IB*	0.35	13.3	0.82	1063	γ, 15

α. A and Q determined from plot of log D *vs.* $1/T$°K.
β. Values of Q taken from reference 8, Fig. 14 and values of A computed from these and Fig. 15.
γ. A and Q determined from Langmuir-Dushman equation.

have been found.)[10] In connection with these ideas, however, the values of Q given in Table II are pertinent. We see that for a given solvent metal Q is greatest for self-diffusion but may decrease to about one-half that value for other chemical elements. If hole diffusion is the dominant process, the energy H should be the same for a given solvent (the concentration of the solute in all cases is small) and therefore all changes in Q should come from J. We are, therefore, forced to assume either that J is at least as large as H and is very sensitive to the nature of the solute or that another process of diffusion is involved. It would seem that calculations of the energies involved in the three theories would be very valuable.

As has been pointed out by many writers, a general trend is noticeable in the values of Q in Table II. This is summed up by saying that for a given solvent metal the activation energy is higher (that is, the diffusion is less) the more nearly the solute is like the solvent. From the tabulation, however, we see that this rule is true only in a very general way and that there is no definite criterion for similarity that is satisfactory. For Si and Sn in Cu two values are given for the ratios of atomic diameters of solute and solvent. The first of these is obtained from the crystal structure of the element and the second, in parentheses, by estimating the "effective size" of the solute atoms in dilute solution in Cu by extrapolating lattice constant *vs.* concentration plots for these alloys[*], [†] to 100 percent solute.

Aid from the Research Corporation to Columbia University in this research is gratefully acknowledged.

APPENDIX

Let us suppose that one unit of isotope is divided between the faces of two quadrants, the individual amounts being, say, a_1 and a_2. Denoting by x_1 and x_2 the depths in the two quadrants and by C_1 and C_2 the concentrations in the sense that C_1dx_1 units of isotope lie between x_1

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[10] E. Koch and C. Wagner, Zeits. f. physik. Chemie **38**, 295 (1937).

[*] Sn in Cu, R. F. Mehl and C. S. Barrett, Trans. A.I.M.M.E. **89**, 203 (1930).

[†] Si in Cu, H. F. Kaiser and C. S. Barrett, Trans. A.I.M.M.E. **93**, 1697 (1931).

and x_1+dx_1, we have the two diffusion equations

$$\partial C_1/\partial t = D\partial^2 C_1/\partial x_1^2 \qquad \text{(A1)}$$

$$\partial C_2/\partial t = D\partial^2 C_2/\partial x_2^2. \qquad \text{(A2)}$$

These equations are true even when the isotope is not spread uniformly in the plane of the surface.

Furthermore if there is evaporation from quadrant 1 to quadrant 2 at a rate R, we must have

$$R = D(\partial C_1/\partial x_1)_{x_1=0} = -D(\partial C_2/\partial x_2)_{x_2=0}. \qquad \text{(A3)}$$

From the experiments described in II, we know that the apparent activity of material lying at a depth y from the surface is reduced by a factor $\exp(-\mu y)$. Hence the combined activity of the two quadrants is

$$F = \int_0^w e^{-\mu x_1} C_1(x_1)dx_1 + \int_0^w e^{-\mu x_2} C_2(x_2)dx_2$$
$$= \int_0^w e^{-\mu x}[C_1(x)+C_2(x)]dx, \qquad \text{(A4)}$$

where w is the thickness of the disk. We see that the essential quantity is $C(x) = C_1(x)+C_2(x)$ and by adding (A1) and (A2) and the parts of (A3) we find

$$\partial C/\partial t = D\partial^2 C/\partial x^2 \qquad \text{(A5)}$$

$$\partial C/\partial x = 0 \quad \text{at } x=0, \qquad \text{(A6)}$$

where C and x may be considered to belong to a single quadrant which does not evaporate.

Calculation of the distribution

We must therefore solve Eq. (A5) subject to the boundary condition (A6) and to a similar boundary condition at $x=w$ and the initial condition that at $t=0$

$$C=0 \quad \text{for} \quad x\neq 0 \quad \text{and} \quad \int_0^w C dx = 1. \qquad \text{(A7)}$$

The solution of the equation can be found by a method of images: one imagines an unbounded slab of material with two units of active isotope on each of the planes $x=0, \pm 2w, \pm 4w, \cdots$. Each of these sources spreads out in the same fashion; the concentration due to the one at $x=2nw$ is

$$u_n = (\pi Dt)^{-\frac{1}{2}} \exp(-(x-2nw)^2/4Dt). \qquad \text{(A8)}$$

The concentration due to such an assembly of sources satisfies the boundary conditions and Eqs. (A5) and (A7). Therefore one form for the solution is

$$C = U = \sum_{n=-\infty}^{+\infty} u_n. \qquad \text{(A9)}$$

This series converges very rapidly if Dt is not much larger than w^2.

For Dt much larger than w^2, a Fourier series solution is more rapidly convergent. The appropriate series is

$$C = V = \sum_{n=0}^{\infty} v_n, \qquad \text{(A10)}$$

where

$$v_0 = 1/w \qquad \text{(A11)}$$

$$v_n = (2/w)\cos(\pi n x/w)\exp(-\pi^2 n^2 Dt/w^2). \qquad \text{(A12)}$$

Calculation of F and B

The above series can be used term by term to calculate F and B according to Eqs. (A4) and the corresponding equation for B given below. We find the results tabulated below:

F with U series:

$$F(z,y) = \int_0^w e^{-\mu x} U dx = \sum_{n=-\infty}^{+\infty} f_{un}, \qquad \text{(A12)}$$

where

$$f_{un} = \int_0^w e^{-\mu x} u_n dx$$
$$= e^{-2ny+z}\left[P\left(\sqrt{z} - n\frac{y}{\sqrt{z}} + \frac{1}{2}\frac{y}{\sqrt{z}}\right) - P\left(\sqrt{z} - n\frac{y}{\sqrt{z}}\right)\right] \qquad \text{(A13)}$$

and P is defined in Eq. (4).

F with V series

$$F(z,y) = \sum_{n=0}^{\infty} f_{vn}, \qquad \text{(A14)}$$

$$f_{v0} = (1-e^{-y})/y, \qquad \text{(A15)}$$

$$f_{vn} = \frac{2y(1-(-)^n e^{-y})}{y^2+\pi^2 n^2} e^{-\pi^2 n^2 z/y^2}. \qquad \text{(A16)}$$

B using *U* series

$$B(z, y)=\int_0^w e^{-\mu(w-x)}Udx=\sum_{n=-\infty}^{+\infty} b_{un}, \tag{A17}$$

$$b_{un}=e^{(2n-1)y+z}\left[P\left(-\sqrt{z}-n\frac{y}{\sqrt{z}}+\frac{1}{2}\frac{y}{\sqrt{z}}\right)\right.$$

$$\left.-P\left(-\sqrt{z}-n\frac{y}{\sqrt{z}}\right)\right]. \tag{A18}$$

B using *V* series

$$B(z, y)=\sum_{n=0}^{\infty} b_{vn}, \tag{A19}$$

$$b_{v0}=(1-e^{-y})/y, \tag{A20}$$

$$b_{vn}=\frac{2y((-1)^n-e^{-y})}{y^2+\pi^2n^2}e^{-\pi^2n^2z/y^2}. \tag{A21}$$

These series have been used in calculating the curves of Figs. 2 and 3; the *U* series used for $z<y^2$ and the *V* series for $z>y^2/9$ the region of overlap serves as a check on the calculations.

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Natural Radioactivity of Lutecium

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The half-life of the natural radioactivity of lutecium reported by Heyden and Wefelmeier is $2.9\pm0.5\times10^{12}$ years for the element or $7.3\pm2\times10^{10}$ years for Lu^{176}, which probably is the active isotope. Negative electrons are emitted. The upper energy limit of the spectrum is 215,000±15,000 electron volts.

THE bearing of the natural radioactivities of the ordinary elements on nuclear physics and geophysics makes it desirable to have data on their characteristics which are as accurate as those for the shorter-lived artificial radioactivities. It is the purpose of this paper to present data obtained on the natural radioactivity of lutecium (cassiopeium) reported by Heyden and Wefelmeier.[1]

The work of Gollnow[2] on the hyperfine structure of lutecium had shown the presence of an unreported isotope of about 2.5 percent abundance. Recently Mattauch and Lichtblau[3] investigated the element with a mass spectrograph and found Lu^{176} present to 2.5 ± 0.07 percent of the element. Since both ytterbium and hafnium have isotopes of mass 176, this makes the Lu^{176} case somewhat similar to that of K^{40} and makes a determination of the sign of the beta-radiation of considerable interest.

The lutecium used was kindly furnished by Professor B. S. Hopkins of the University of Illinois. It was pure except for traces of thulium and ytterbium.

PROOF THAT THE ACTIVITY BELONGS TO A RARE EARTH ELEMENT

A consideration of the possible impurities (other than elements of low atomic number which would have to be present in large amounts to affect the data) reveals that all of those emitting beta-radiation of approximately the same

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