Equation (13) can be written:

$$p = 2(R^2 - \theta)[\gamma/2]^{\frac{1}{3}},$$

where

$$R = u'/u.$$

From the condition at the initial boundary $R_0 \simeq Ai'(\theta_0)/Ai(\theta_0)$ can be easily calculated. θ_0 can be found then from the table. For the end boundary, $\theta_2 = \theta_0 + l[\gamma/2]^{\frac{1}{3}}$, we can similarly calculate $R_2 = u'(\theta_2)/u(\theta_2)$ from p_2. Since

$$u'(\theta_2)/u(\theta_2) = [Ai'(\theta_2) + (B/A)Bi'(\theta_2)]/$$
$$[Ai(\theta_2) + (B/A)Bi(\theta_2)],$$

taking the values of $Ai(\theta_2)$, $Ai'(\theta_2)$, $Bi(\theta_2)$, and

$Bi'(\theta_2)$ from the table, the value of B/A is readily calculated. The term involving B/A is significant only in the immediate neighborhood of the end boundary. It serves to adjust the boundary value of p. Since it becomes negligible for small values of $\Delta\theta = \theta_2 - \theta$ a large p_2 results only in a sharp rise of p near the very boundary. The density of electrons over most of the layer is not much affected by the value of p_2 (all this is for large v). The dashed lines joining the curves of v at the end boundary in Fig. 2 is calculated by neglecting the term involving B/A. We see that for $v > 40$ neglecting this term will involve little error.

On the Theory of Vacancy Diffusion in Alloys

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(Received July 12, 1948)

The theory of diffusion in alloys is discussed on the basis of the migration of lattice vacancies in an attempt to interpret the experiments of W. A. Johnson on diffusion in gold-silver alloys. It is assumed that the lattice network preserves its identity during the diffusion even though there is a resultant vacancy current passing through any region. It is also assumed that two types of atom, designated as A and B atoms, are present in the lattice. The diffusion coefficients are expressed in terms of a function $p(n_{a1}, n_{a2})$ giving the probability that a vacancy in jumping from one atomic plane (designated as plane 2) to a neighboring plane (designated as plane 1) will interchange places with an A atom if there are n_{a1} A atoms per unit area of plane 1 and n_{a2} A atoms in plane 2. It is found that the chemical diffusion coefficient is related to the function p in a very different way from the diffusion coefficients for radioactive tracers if the latter migrate when no chemical gradient is present. Models of increasing complexity are employed to derive explicit expressions for the function p. It is found that Johnson's experiments can be explained only with the use of models that are more complex than those commonly used. The theory of vacancy diffusion is also employed to interpret the experiments of Smigelskas and Kirkendall concerning the relative displacement during diffusion of fiducial markers placed at the interface between copper and brass. An experiment which could provide an absolute test for vacancy diffusion is proposed.

I. INTRODUCTION

THE experiments of W. A. Johnson[1] on the diffusion in 50–50 gold-silver alloys have raised an interesting question concerning the theory of diffusion in alloys. Johnson investigated the rate at which radioactive silver and gold atoms diffuse in the alloy as well as the rate at which a minor gradient in composition is made uniform. The system studied is rather an ideal one because the constituent atoms combine substitutionally over the entire range of composition in the face-centered cubic system and do

not seem to exhibit the development of long range order at particular compositions, as in the copper-gold system. The specimens on which measurements were made contained planar gradients of the diffusing atoms, so that only one Cartesian variable enters in the diffusion equation.

Figure 1 shows the measured diffusion coefficients when plotted as functions of temperature. As is conventional in the field, the logarithm of the diffusion coefficient is plotted as a function of the reciprocal of the absolute temperature. The upper curve represents D_c, the diffusion coef-

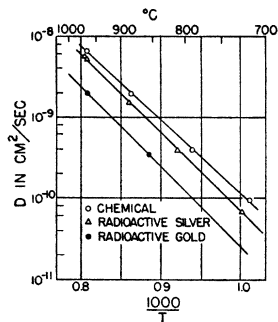[1] W. A. Johnson, Trans. A.I.M.M.E. **147**, 331 (1942).

Fig. 1. The diffusion coefficients in the 50–50 silver-gold system (after Johnson). D_c is the chemical diffusion coefficient; D_{Ag} and D_{Au} are the coefficients for diffusion of radioactive tracers of silver and gold measured in a system in which there is no chemical gradient. The logarithm of the diffusion coefficient is plotted as a function of the reciprocal of the absolute temperature.

ficient that governs the rate at which a gradient in chemical composition is smoothed. In determining this Johnson used in conjunction specimens of two alloys in the 50–50 range of composition having about 14 percent of difference in concentration of the constituents. The second and the lowest curves depict the diffusion coefficients for migration of radioactive silver and gold, respectively. The coefficients were measured by using pairs of specimens which had identical chemical composition; however, one member contained a radioactive tracer.

Johnson found that the best straight lines which would fit the experimental points corresponded to the relations:

$$D_c = 0.14 \exp(-41,700/RT) \text{ cm}^2/\text{sec.},$$
$$D_{Ag} = 0.39 \exp(-44,700/RT) \text{ cm}^2/\text{sec.}, \quad (1)$$
$$D_{Au} = 0.12 \exp(-44,100/RT) \text{ cm}^2/\text{sec.}$$

The activation energies appearing in these equations are expressed in cal./mole. R is the gas constant. The fact that the activation energies are not quite equal implies that the best straight lines passing through the points of Fig. 1 are not quite parallel.

If we were to assume that all three activation energies actually are equal, and arbitrarily chose the common value to be that for gold, namely, 44,100 cal./mole, the corresponding functions would be

$$D_c = 0.41 \exp(-44,100/RT),$$
$$D_{Ag} = 0.30 \exp(-44,100/RT), \quad (2)$$
$$D_{Au} = 0.12 \exp(-44,100/RT).$$

Thus the measured value of D_c is approximately 1.4 times larger than the value of D_{Ag} and approximately 3.5 times larger than D_{Au}. It is evident from Fig. 1 that this conclusion is quite independent of the question of whether the activation energies are equal or slightly different.

It is difficult to visualize, at first glance, the circumstances which might make it possible for the chemical diffusion coefficient to be larger than those for radioactive tracers, yet it is not apparent that this could not be the case. This topic has been discussed by several investigators,[2] most notably Darken.[3]

Darken has assumed that each atomic constituent of the lattice has its own characteristic diffusion coefficient and that the structure manages by an unspecified form of mass motion to keep the density of atoms per unit volume constant in spite of the fact that one type of atom may be diffusing in or out of a given region of the specimen more rapidly than other atoms diffuse out of or into it. If, for example, the system is a binary alloy and if A atoms are diffusing out of a given volume more rapidly than B atoms diffuse into it, the volume would contract in such a way as to maintain constant density. This type of contraction or expansion would impart a material velocity v to any atom or object in the lattice which does not participate in the diffusion. Since the local velocity of flow must be such as to compensate for the net difference in flow of atoms by diffusion, Darken is able to relate the velocity v to the diffusion currents. If D_a and D_b are the diffusion coefficients for the two constituent atoms, the velocity of flow at a given point in the specimen is

$$v = (D_a - D_b)\frac{\partial f_a}{\partial x}, \quad (3)$$

where f_a is the fractional concentration of A atoms. It is assumed that the concentration gradient is along the x axis. The axis of reference is chosen so that the velocity vanishes at regions of the specimen where the concentration gradient

[2] C. E. Birchenall and R. F. Mehl, Trans. A.I.M.E. **171** (1947); J. C. Fisher and J. H. Hollomon, Metals Tech., Tech. Pub. 2344 (1948).
[3] L. S. Darken, Metals Tech., Tech. Pub. 2311 (1948).

is zero. Darken's diffusion equation is

$$\frac{\partial f_a}{\partial t} = \frac{\partial}{\partial x}\left[(f_aD_a+f_bD_b)\frac{\partial f_a}{\partial x}\right],\qquad(4)$$

so that

$$D=(f_aD_a+f_bD_b)\qquad(5)$$

plays the role of the chemical diffusion coefficient.

The key assumption of Darken's treatment is that the metal can swell or shrink in a more or less plastic manner to compensate for unbalanced diffusion, maintaining constant atomic density thereby. If diffusion occurs by the migration of vacancies in the alloys of interest, it is conceivable that shrinking could occur by condensation of vacancies in a local region to form small plate-like voids which draw themselves together and disappear by inducing plastic flow in the surrounding metal in much the way that voids can be closed by pressing a ductile substance. In a polycrystalline mass the vacancies could "condense" at grain boundaries. If diffusion occurred by migration of interstitial atoms, a swelling could be induced in a region by precipitation of interstitial atoms which have diffused to the volume. The precipitate might induce a plastic expansion to compensate almost exactly for the volume of precipitated matter.

In tentative support of his viewpoint, Darken calls attention to a very interesting set of experiments of Smigelskas and Kirkendall.[4] These investigators studied the migration of the boundary between 70–30 alpha-brass and copper. An accurately shaped rectangular bar of brass was plated with a thick coating of copper on all four lateral surfaces in such a way that a number of small molybdenum wires were imbedded at the interface between the metals. It was found that after diffusion had been allowed to take place the spacing between wires on opposite rectangular faces was smaller than before diffusion by a much larger amount than could be accounted for by normal change of lattice parameter with composition. The change in spacing when plotted as a function of the square root of the time of diffusion is shown in Fig. 2. Smigelskas and Kirken-

dall noted that the original boundary between the two metals was clearly marked by non-metallic inclusions which, like the molybdenum wire, presumably did not enter into the diffusion process. These inclusions moved with the molybdenum wire. The experiments also show that the amount of zinc on the copper side of the boundary after diffusion is greater than the amount of copper that has diffused into the brass side by just about the amount needed to explain the contraction if the atomic density remained constant.

From Darken's viewpoint, Smigelskas and Kirkendall's results are to be explained by assuming that zinc diffuses out of the brass more rapidly than copper diffuses into it. In consequence, the brass core shrinks in the manner described above, pulling the molybdenum wires and other fiducial marks at the initial grain boundary with it. Darken has shown that his equations give an adequate description of the effect if proper values for the diffusion coefficients for copper and zinc are assumed.

The purpose of the present paper is to attempt to shed more light on Johnson's experiments with the use of a more explicit mechanism of diffusion than that employed by Darken. It will be assumed that all of the measurable mobility in the silver-gold alloy is the result of vacancy diffusion, that is, that a given atom can move from one site to another only when a vacant lattice site appears among its neighbors and the given atom jumps into this vacant neighboring position. The calculations of Huntington[5] and
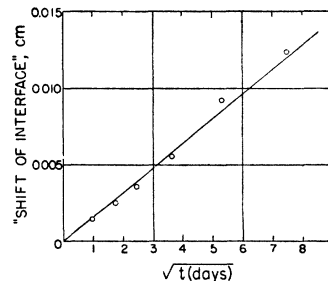

FIG. 2. The contraction of the region within the fiducial markers of molybdenum in the experiments of Smigelskas and Kirkendall. The contraction is plotted as a function of the square root of the time.

[4] A. D. Smigelskas and E. O. Kirkendall, Trans. Am. Inst. Min. Met. Eng. 171, 130 (1947). The earliest experiments of this type of which the writer is aware were carried out by W. Shockley in 1938. Shockley observed a displacement of the type found by Smigelskas and Kirkendall.

[5] H. B. Huntington and F. Seitz, Phys. Rev. 61, 315, 325 (1942).

the writer on this topic for the case of copper seems to leave little doubt that the vacancy mechanism is strongly preferred over the "direct interchange" or interstitial diffusion mechanisms, at least in the case of the metals having large inner shells. In any case, the vacancy mechanism is at least as complex as the other two and hence should permit as intricate processes as the other two. In fact it offers a greater range of permissible phenomena than the direct interchange mechanism, since the latter does not permit a net flow of atoms across any boundary.

We shall see that it actually is possible to envisage a model in which the chemical diffusion coefficient is larger than the diffusion coefficients for radioactive tracers. On the other hand, it is not possible to explain Johnson's results with the more obvious models of a binary alloy that might be employed to simulate an actual case.

To simplify the situation we shall assume that the concentration gradient, whether a chemical gradient or that of a tracer, depends only on one Cartesian variable which will be taken to be the x coordinate. Without loss of generality we may also assume that well defined crystallographic planes separated by distance λ lie normal to the x axis. Since we shall be primarily interested in cases of very high symmetry, we shall assume that neighboring crystallographic planes of this well defined type are symmetrically equivalent, that is, can be sent into one another by means of one of the symmetry elements of the lattice.

Whenever we discuss a practical diffusion experiment, it will be assumed that the specimen consists of two halves which individually have uniform concentration at start; however, the initial concentration in each half will differ. The two halves of the specimen will meet at an essentially infinite plane that coincides with the plane $x=0$. It will be assumed that the specimens extend for a very large distance along the x axis, so that all surfaces other than the two in contact can be treated as if at infinite distance. If the concentration of migrating atoms satisfies the conventional diffusion equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} D \frac{\partial c}{\partial x}, \quad (6)$$

the solution appropriate to the boundary con-

ditions described above for the hypothetical experimental specimen consisting of two infinite halves in planar contact is

$$c(x, t) = c_1 + \frac{(c_2 - c_1)}{(\pi)^{\frac{1}{2}}} \int_{-\infty}^{x/2(Dt)^{\frac{1}{2}}} \exp(-\alpha^2) d\alpha, \quad (7)$$

when D is a constant. Here c_1 is the initial uniform concentration $(t=0)$ for the half of the specimen lying on the negative side of the x axis, and c_2 is the initial concentration on the positive side of the axis. This solution depends on x and t only through the combination x^2/Dt, a fact which remains valid in the case of planar symmetry even when D in (6) is a function of concentration.

II. THE DIFFUSION CURRENTS

Let us designate the chemical species present in the alloy by A and B, and assume that in any given crystallographic plane there are $n_a A$ atoms and $n_b B$ atoms per unit area. If there are n atomic sites per unit area of the plane we shall have the relation

$$n_a + n_b + n_v = n, \quad (8)$$

where n_v is the number of vacant sites per unit area. We shall assume that n_v is very small compared to n_a and n_b, so that the relation

$$n_b = n - n_a \quad (9)$$

can be used to determine the density of B atoms from the density of A atoms if the latter is given. This assumption is justified by the fact that the density of vacant lattice sites is probably small even at the melting point. The calculations for copper indicate that the energy required for formation of a vacancy is of the order of 1.8 ev. In any case the fraction of vacant sites probably is not larger than 10^{-3} at the melting point in the metals of interest to us.

Let us focus attention on a region of the alloy in which there is a small gradient in concentration of A atoms (and hence of B atoms) or a gradient in a radioactive tracer. We shall assume that there is a uniform current of vacancies through this region, the direction of flow being the same as the direction of the concentration gradient, namely, the x direction. The mobility of vacancies is so much greater than the mobility of atoms

that a concentration gradient in vacancies that exists in a specimen in which diffusion is being studied will tend to decrease much more rapidly than a concentration gradient in the distribution of atoms. As a result, the vacancy current which exists in any region of the specimen after a period of time will be the result of flow of vacancies from relatively widely separated regions in which differences in concentration exist. In this connection it is to be noted that when two specimens of an alloy, which are individually uniform but contain slight differences in composition, are brought together the thermodynamic potential of the vacancies in each specimen will be equal if the specimens are individually at equilibrium. As a result there would be, at least initially, no reason for a vacancy current to flow. As the chemical diffusion takes place there may be a tendency for vacancies to diffuse to or away from the zone in which chemical interdiffusion has occurred, because the equilibrium density of vacancies in this region may be different from the density which existed there initially. This flow will presumably be small because the total number of vacancies involved will be small if the zone of interdiffusion is small. It seems safe to conclude that a large vacancy current will be present only if the vacancies are not at equilibrium initially in one or both halves of the specimen, in which case there will be a stream of vacancies moving through a large part of the system.

Consider two neighboring crystallographic planes which are normal to the x axis. We shall call the plane on the negative side number 1 and the plane on the positive side number 2 (Fig. 3). The density of A atoms in each plane will be designated by n_{a1} and n_{a2}. Now suppose that ν_{12} vacancies are jumping from plane 1 to plane 2 per unit area in unit time, and that a number ν_{21} are jumping in the reverse direction. The vacancy current in the positive x direction will then be $\nu_{12} - \nu_{21}$. If $p(n_{a1}, n_{a2})$ is the probability that a vacancy in jumping from plane 2 to plane 1 will jump into the site occupied by an A atom, and if $p(n_{a2}, n_{a1})$ is the probability that a vacancy will replace an A atom in a jump in the reverse direction, the current of A atoms between planes is

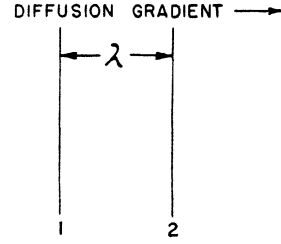$$I_a = \nu_{21}p(n_{a1}, n_{a2}) - \nu_{12}p(n_{a2}, n_{a1}). \quad (10)$$

DIFFUSION GRADIENT ⟶

FIG. 3. Two consecutive planes in the direction normal to the diffusion gradient. The density of atoms in the planes is designated by n. λ is the spacing between planes.

Since n_{a1} and n_{a2} are nearly equal, we shall expand $p(\xi, \eta)$ in the manner

$$p(n_{a1}, n_{a2}) = p(n_a, n_a) - \frac{\partial p}{\partial \xi}\frac{\partial n_a}{\partial x}\frac{\lambda}{2} + \frac{\partial p}{\partial \eta}\frac{\partial n_a}{\partial x}\frac{\lambda}{2},$$

$$p(n_{a2}, n_{a1}) = p(n_a, n_a) + \frac{\partial p}{\partial \xi}\frac{\partial n_a}{\partial x}\frac{\lambda}{2} - \frac{\partial p}{\partial \eta}\frac{\partial n_a}{\partial x}\frac{\lambda}{2}.$$

$$(11)$$

Here $n_a = (n_{a1} + n_{a2})/2$ is the average density of A atoms in the two planes. The derivatives $\partial p/\partial \xi$ and $\partial p/\partial \eta$ are evaluated for $\xi = \eta = n_a$, and λ is the separation of the two planes. When the relations (11) are substituted in (10) we obtain

$$I_a = -I_v p(n_a) - (\nu_{12} + \nu_{21})\frac{\lambda}{2}(\alpha - \beta)\frac{\partial n_a}{\partial x}, \quad (12)$$

where

$$p(n_a) \equiv p(n_a, n_a), \quad \alpha \equiv \frac{\partial p}{\partial \xi}, \quad \beta \equiv \frac{\partial p}{\partial \eta}$$

$$(\xi = \eta = n_a). \quad (13)$$

Since the volume concentration of A atoms in the neighborhood of the two planes, c_a, is n_a/λ, I_a may be expressed in the form

$$I_a = -I_v p(n_a) - D_a\frac{\partial c_a}{\partial x}, \quad (14)$$

where

$$D_a = (\nu_{12} + \nu_{21})\frac{\lambda^2}{2}(\alpha - \beta). \quad (15)$$

Now

$$\frac{\partial c_a}{\partial t} = -\mathrm{div}I_a = I_v\frac{dp(n_a)}{dn_a}\frac{\partial n_a}{\partial x} + \frac{\partial}{\partial x}D_c\frac{\partial c_a}{\partial x}, \quad (16)$$

provided I_v is independent of position (but not necessarily of time) in the region considered. If the variation in concentration is relatively small

in the specimen, $dp(n_a)/dn_a$ may be treated as a constant. We note that this equation may be transformed to the form

$$\frac{\partial c_a}{\partial t}=\frac{\partial}{\partial x}D_a\frac{\partial c_a}{\partial x} \qquad (17)$$

by means of the transformation

$$x'=x+vt, \quad t'=t, \qquad (18)$$

where

$$v=I_v\lambda dp(n_a)/dn_a, \qquad (19)$$

provided I_v is independent of time as well as position, so that v is a constant. Thus the motion of the A atoms is a superposition of a drift with uniform velocity v given by (19) in the negative x direction and diffusion with the diffusion coefficient D_a, when I_v is constant.

A similar analysis of the migration of B atoms shows that the current of B atoms, I_b, satisfies the equation

$$I_b=-I_v(1-p(n_a))+D_a\frac{\partial c_a}{\partial x}, \qquad (20)$$

where $(1-p(n_a))$ is the probability that a vacancy will jump into the site occupied by a B atom when the planar density of A atoms is the same in neighboring planes and has the value n_a. Since $\mathrm{div}I_b=-\mathrm{div}I_a$ when I_v is constant, it is clear that (20) may be transformed into (16). Moreover, since the time and space derivatives of c_a are the negative of those of c_b, the volume concentration of B atoms, it follows that the migration of B atoms is also governed by the superposition of a uniform velocity v in the $-x$ direction and diffusion with diffusion coefficient D_a.

Consider next the migration of radioactive A atoms. We shall assume that the specimen has uniform chemical composition except for the fact some of the normal A atoms are replaced by radioactive atoms. If n_{a1}^* and n_{a2}^* are the concentrations of radioactive atoms in the two neighboring planes described above, the current of radioactive atoms is

$$I_a^*=\nu_{21}p(n_a)\frac{n_{a1}^*}{n_a}-\nu_{12}p(n_a)\frac{n_{a2}^*}{n_a}$$
$$=-I_vp(n_a)\frac{n_a^*}{n}-D_a^*\frac{\partial c_a^*}{\partial x}, \qquad (21)$$

where

$$D_a^*=(\nu_{12}+\nu_{21})\frac{\lambda^2}{2}\frac{p(n_a)}{n_a}, \qquad (22)$$

and c_a^* is the volume concentration of radioactive atoms. It follows that the migration of the radioactive atoms is the superposition of a uniform motion with velocity $v^*=I_v\lambda p(n_a)/n_a$ and diffusion with the diffusion coefficient D_a^* when I_v is constant. The corresponding diffusion coefficient for radioactive B atoms is

$$D_b^*=(\nu_{12}+\nu_{21})\frac{\lambda^2}{2}\frac{(1-p(n_a))}{n_b}, \qquad (23)$$

where n_b is the planar density of B atoms.

It is evident from the form of (14) and (20) that D_a is the quantity that should be designated as the chemical diffusion coefficient and may be called D_c in the following.

III. MIGRATION OF DIFFUSION BOUNDARY

Before considering the differences between the diffusion coefficients derived in the previous section, it is fruitful to contemplate the effects of a steady vacancy current in somewhat more detail.

If the mathematical framework of lattice points between which the atoms jump could be regarded as rigidly fixed, fiducial inclusions, such as the molybdenum wires employed in the experiments of Smigelskas and Kirkendall, which do not participate in diffusion would remain fixed relative to the framework and provide an origin for the stationary x coordinate. We shall keep this possibility in mind in the ensuing discussion.

The fact that the diffusing atoms experience a uniform drift as well as Brownian migration when there is a constant vacancy current is not surprising. If this current is present, the initial boundary plane between two specimens will cease to be the plane at which the concentration is just half-way between the initial values in the two halves of the specimen when D is constant (see solution (7)). Instead, this intermediate plane will be displaced by a distance vt at the end of time t in the case of chemical diffusion or by v^*t in the case of radioactive diffusion.

If the initial difference in composition of the two halves of the specimen is relatively large,

$dp(n_a)/dn_a$ in (19) will not be independent of position, and the drift motion of the atoms resulting from the vacancy current will be a function of position. We shall consider this case in conjunction with that in which I_v varies with time.

Suppose that the vacancies in the two halves of a specimen have different chemical potentials so that a vacancy current flows across the boundary when diffusion begins. We shall assume that the vacancies diffuse in accordance with Eq. (6), D being replaced by the appropriate diffusion coefficient in each half of the specimen, and c being the concentration of vacancies. We shall assume that the diffusion coefficient for vacancies is several orders of magnitude larger than D_c, D_a^*, or D_b^*, so that a uniform vacancy current is established in the boundary region where chemical or radioactive diffusion occurs before appreciable chemical or radioactive diffusion has taken place. This current, though uniform throughout the interesting region of space, will not be constant in time. It may readily be shown that the interesting solution for the concentration of vacancies depends upon position and time through a factor $x/(t)^{\frac{1}{2}}$, so that the vacancy current varies as $1/(t)^{\frac{1}{2}}$ at the boundary where chemical or radioactive diffusion is occurring. In this case, the equations of the form (16) and (21) may be written as

$$\frac{\partial c}{\partial t} = \frac{\mu \partial c}{(t)^{\frac{1}{2}} \partial x} + \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right). \qquad (24)$$

As previously c is the concentration of the diffusing atoms, D is the appropriate diffusion coefficient and μ is a quantity independent of time and postion. Both D and μ may depend upon the composition. They may be treated as constants in radioactive diffusion if the two halves of a specimen have the same chemical composition. Their dependence on composition is important in chemical diffusion if the initial difference in composition of the halves of the specimen is sufficiently great. The $(t)^{\frac{1}{2}}$ appearing in the denominator of the first term on the right arises from the dependence of I_v on time described above.

Equation (24) may be expected to possess a solution that satisfies the boundary conditions of

interest to us and is purely a function of the variable $s = x/(t)^{\frac{1}{2}}$. The corresponding function $c = f(s)$ satisfies the ordinary equation

$$-\frac{(s+2\mu)}{2}\frac{df}{ds} = \frac{d}{ds}\left(D\frac{df}{ds}\right), \qquad (25)$$

in which D and μ may be functions of f in the general case.[6] The interesting solution of this equation when D and μ are constants is

$$f = c_1 + (c_2 - c_1)\int_{-\infty}^{s'/2(D)^{\frac{1}{2}}} \frac{\exp(-\alpha^2)d\alpha}{(\pi)^{\frac{1}{2}}} \qquad (26)$$

in which $s' = s + 2\mu$ and c_1 and c_2, as previously, are the initial concentrations in the two halves of the specimen. We see that the point at which the concentration is $(c_1 + c_2)/2$ is at the position where $s' = 0$ or at $x = -2\mu(t)^{\frac{1}{2}}$ at time t. Relative to a moving origin chosen at this point, the diffusion is exactly as if there were no net vacancy current.

In the more general case in which D and μ are functions of concentration, $f(s)$ will range between c_1 and c_2 as s varies from $-\infty$ to $+\infty$. As long as the concentration difference is not large we may expect to find a value of s for which $f = (c_1 + c_2)/2$. If D and μ were constant so that the solution (26) were valid, this point would be $s = 2\mu$. Moreover, the function df/ds would be symmetrical about this point, so that d^2f/ds^2 would be zero when $s = 2\mu$. In the general case in which neither D nor μ are constants we may expect none of these simple relations to hold: usually the df/ds curve will not be symmetrical about the point for which $f = (c_1 + c_2)/2$, nor will d^2f/ds^2 vanish there.

At infinitesimal times after the start of diffusion, the point at which the concentration is $(c_1 + c_2)/2$ will be at the initial interface. Relative to the initial lattice network, it will be at a position $x_i = s_i(t)^{\frac{1}{2}}$ at time t. It is clear that the coefficient s_i will depend both upon the concentrations c_1 and c_2 and upon the accidental difference in initial concentration of vacancies in the two halves of the specimen.

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[6] The solutions of (25) may be classified in the following manner: Given $f = a$ and $df/ds = b$ for a specified value of s, Eq. (25) may be integrated to obtain values of $f(+\infty) = c_2$ and $f(-\infty) = c_1$. These values of c_1 and c_2 may be regarded as functions of a and b, which can in turn be inverted to yield a and b in terms of c_1 and c_2.

The initial interface, for which x is zero and which, at least in principle, may be marked by fiducial material, corresponds to the point $s = 0$. The concentration at this point remains constant as diffusion proceeds according to the present treatment of the problem. This result, which agrees with the experiments of Smigelskas and Kirkendall, was also obtained by Darken on the basis of his formulation of diffusion, and evidently depends only on the fact that the concentration can be expressed as a function of $x/t^{\frac{1}{2}}$.

The shift of the fiducial markers observed by Smigelskas and Kirkendall in the copper-brass remains to be discussed. If the mathematical formulation given in the preceding section were strictly correct, there would be no room for a displacement of the type found by these investigators, apart from the effect of change in lattice parameter with composition. Each atom which moves out of the central core within the initial copper-brass boundary would be replaced either by another atom or by a vacancy, which would have almost the same atomic volume as one of the atoms of the alloy. As a result the fiducial boundary would remain fixed, or two such boundaries on opposite sides of the core would not move relative to one another by more than the distance associated with change in lattice parameter. In order to explain the observed results with the use of vacancy theory, it apparently is necessary to adopt the following viewpoint: vacancies diffuse from the electroplated copper into the brass, permitting a net flow of zinc and copper atoms across the boundary separating the brass from the copper. It is possible that the copper, being an electroplated deposit, contains a high density of voids and hence of vacancies at start. In any event the vacancies could diffuse from the vacuum interface if needed. The vacancy current should vary as $1/t^{\frac{1}{2}}$ at least initially, for reasons described earlier, so that the total number of vacancies which would have flowed past the boundary at the end of time t would vary as $t^{\frac{1}{2}}$. As long as the vacancies in the brass remain atomically dispersed, the fiducial lines do not shift relative to one another. However, as the specimen is cooled, the vacancies condense to form voids. These voids close, at least in part, as a result of the action of surface tension forces and plastic flow,

and the fiducial markers are drawn together. If the contraction in volume compensates for the vacancies which have diffused, this contraction should vary as $t^{\frac{1}{2}}$. Since free energy is to be gained by having zinc migrate into the copper to form a more dilute alloy of brass, it is conceivable that the vacancy current would supersaturate the brass during diffusion and that the condensation of vacancies with the consequent sintering would actually occur during diffusion.[7] These two cases could be distinguished, at least in principle, by observing whether the displacement of the boundary occurs during diffusion or subsequently.

The preceding picture of the displacement of the boundary does not appear at first sight to be substantially different from Darken's. Actually, there are several differences. Darken's formulation explicitly assumes that the contraction takes place in the region where the chemical concentration gradient is greatest. That given here permits the contraction to occur over the entire zone through which vacancies migrate. If the diffusion coefficient for vacancies is 10^3 times larger than that for atoms, this zone may be thirty times larger than the zone in which chemical diffusion has occurred. Thus the contraction within the region where the chemical gradient is large may be a negligible fraction of the whole.

In this connection, Smigelskas and Kirkendall state that after diffusion "the brass to the right of the interface is particularly susceptible to pitting. This is the side from which the zinc is diffusing to the left faster than the copper is diffusing to the right." They conclude the pitting is associated with voids induced during diffusion. Presumably these voids are the condensed gas of vacancies. Unfortunately the experimenters do

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[7] In the discussion of the paper by Smigelskas and Kirkendall, C. S. Smith has suggested that the volume changes accompanying diffusion create cracks in the brass core which run normal to the interface and which promote diffusion by permitting zinc to migrate from the brass by gaseous diffusion. It is postulated that these cracks sinter together at a later period of time and thereby account for the loss of volume of the core. Although this suggestion does not explain the way in which the zinc succeeds in migrating into the copper to cause the stresses which are assumed to exist, it is possible that the presence of zinc vapor and the gradual sintering of voids would have the effect of inducing vacancies to diffuse continuously from outside the specimen, thereby creating a continuous vacancy current.

not describe the width of the zone in which the pitting occurs.

Smigelskas and Kirkendall found that the contraction of the inner core of the diffusion specimen represented about one percent of the linear dimensions at the end of 56 hours of diffusion at 785°C. The zone of chemical diffusion then represented about 20 percent of dimensions of the core. It follows that approximately one percent of the atoms of the core would have been replaced by vacancies, according to the picture presented here. It is hardly likely that all of these vacancies would have initiated in the electroplated copper —most must have come from the outer interface of the specimen. One might expect vacancies to have diffused throughout the core before 56 hours have elapsed and hence to observe a deviation from the rule that I_v varies as $t^{-\frac{1}{2}}$. The fact that this deviation does not seem to be observed (Fig. 2) remains to be explained if the vacancy mechanism is correct.

Another difference between the interpretation based on vacancies and that implied in Darken's theory is made clear by considering an experiment identical with Smigelskas and Kirkendall's, except that the copper and brass are interchanged. If Darken's viewpoint is correct the copper core should swell, since zinc atoms would diffuse into it more rapidly than copper diffuses out. On the other hand, if the vacancy mechanism of diffusion is valid the fiducial markings about the core should either remain unchanged if the vacancy current is zero, or should pull together, much as in the experiment in which there is a brass core, *provided* the only source of vacancies for an extended amount of diffusion lies outside the specimen. It would be highly interesting to see the results of an experiment of this kind.

IV. COMPARISON OF DIFFUSION COEFFICIENTS

Equations (15), (22), and (23) represent the diffusion coefficients of interest for Johnson's experiments. The following points are worthy of note:

(a) The diffusion coefficients will be influenced by any deviation of the density of vacancies from the equilibrium value for the pure alloy. This effect, which will influence $\nu_{12}+\nu_{21}$, is well known from the studies of electrolytic conduction

in the salts in which the density of vacancies may be suppressed or raised by additive agents.

(b) The expressions for D_c and for the radioactive diffusion coefficients are intrinsically different in form. The first involves derivatives of the coefficient $p(\xi, \eta)$ which determines the probability that a vacancy will land on an A atom in jumping from one plane to the next, whereas the second involves $p(n_a, n_a)$ alone. In the case of 50–50 composition $(n_a = n_b = 1 - n_a)$ the sum of D_a^* and D_b^* is

$$D_a^* + D_b^* = (\nu_{12} + \nu_{21})\frac{\lambda^2}{n_a}, \qquad (27)$$

which does not involve p.

The writer has not been able to derive relations between $p(n_a)$ and the derivatives α and β which are independent of special models that are used to describe diffusion. It appears that there are no general rules governing the behavior of $p(\xi, \eta)$ other than that it be equal to unity when $\xi = n$, where n is the density of atoms in a plane normal to the gradient, and be zero when $\xi = 0$.

In principle, $p(n_a)$ could be determined as a function of n_a by measuring the diffusion of radioactive A or B atoms for various compositions. A determination of this type would require knowledge of $(\nu_{12}+\nu_{21})$; however, let us assume that this offers no problem. Three conceivable forms of $p(n_a)$ are shown in Fig. 4. These are selected somewhat arbitrarily to indicate possible situations. Curve I, which is a straight line, could occur if A and B atoms were almost identical
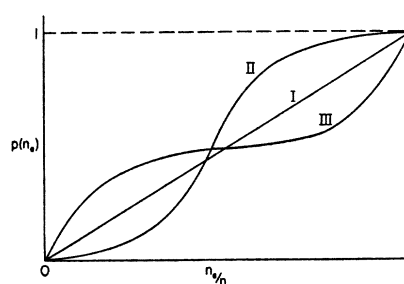

FIG. 4. Schematic representation of $p(n_c)$ in three interesting cases. Case I is that which would be valid in an ideal two-component alloy in which the atoms behaved as if chemically identical. Case II is a hypothetical one in which the slope is very steep in the 50–50 range of composition, whereas Case III is one in which the slope is small. The abscissa is n_a/n, the fraction of A atoms in each plane. The curves are constrained to pass through the points zero and unity at the two ends by definition.

chemically so that $p(n_a) = n_a/n$. Now the slope of any of these curves at a given point is readily seen to be $\alpha + \beta$ for $\xi = \eta = n_a$. Suppose that β is very small compared with α, a situation that need not occur generally, but which will obtain if the A and B atoms are very similar. In this case the slope of the $p(n_a)$ curve in Fig. 4 determines α and hence determines the quantity $(\alpha - \beta)$ appearing in D_c (Eq. (15)). A straightforward analysis of the three curves under these simplifying assumptions shows that in the vicinity of 50–50 composition $D_c = D_a^*$ in case I, $D_c > D_a^*$ in case II, and $D_c < D_a^*$ in case III. D_c may be larger than the sum of D_a^* and D_b^* for the 50–50 composition if the slope of the $p(n_a)$ curve is greater than 2, as is possible in case II.

V. A SIMPLE MODEL OF A DIFFUSING SYSTEM

It is interesting to consider the workings of a simple model of a system in which diffusion is occurring in order to visualize a case in which the radioactive and chemical diffusion coefficients are not identical. The results obtained from a specialized model evidently will lack generality. This disadvantage is compensated for by the fact that they are explicit.

Let us consider a case in which there is a constant gradient of concentration in the x direction and in which a given atom in one of the planes perpendicular to the x axis has only one neighboring site in the adjacent plane into which it could jump by vacancy diffusion. This would be the case in a simple cubic lattice if vacancies could jump only along the directions of the cube edges. We shall assume that the atoms interact in pairs and that the probability that an A atom in a given plane, which we shall designate the 1 plane, will have a vacancy in the neighboring site in an adjacent plane, designated the 2 plane, is

$$P_a(1, 2) = C_{12} \exp(-V_a/kT)\frac{n_{v2}}{n}, \qquad (28)$$

in which C_{12} is a coefficient which depends upon the composition, V_a is an energy parameter representing the average relative change in energy of a lattice induced by placing a vacancy next to an A atom, n_{v2} is the density of vacancies in the

2 plane, and n is the density of atoms in the planes normal to the x axis. Similarly, we shall assume that the corresponding probability for a B atom in the 1 plane is

$$P_b(1, 2) = C_{12} \exp(-V_b/kT)\frac{n_{v2}}{n}. \qquad (29)$$

From the condition

$$n_{a1}P_a(1, 2) + n_{b1}P_b(1, 2) = n_{v2}, \qquad (30)$$

we find

$$C_{12} = \frac{n}{n_{a1} \exp(-V_a/kT) + n_{b1} \exp(-V_b/kT)}. \qquad (31)$$

It is readily seen that under these assumptions $P_a(1, 2)$ and $P_b(1, 2)$ involve the energies V_a and V_b only through the factor

$$f = \exp(-(V_a - V_b)/kT). \qquad (32)$$

If ν_{21} vacancies are jumping per unit time per unit area from plane 2 to plane 1, and if $p(n_{a1}, n_{a2})$, as in Section II, is the probability that a given vacancy will land on an A atom, we obtain the relations

$$\nu_{21}p(n_{a1}, n_{a2}) = \nu_a n_{a1}P_a(1, 2), \qquad (33)$$

$$\nu_{21}(1 - p(n_{a1}, n_{a2})) = \nu_b n_{b1}P_b(1, 2), \qquad (34)$$

in which ν_a is the probability per unit time that a vacancy which is next to an A atom will change places with it, and ν_b is the corresponding probability for interchange of a vacancy with a neighboring B atom. By adding (33) and (34) we obtain

$$\nu_{21} = C_{12}\frac{n_{v2}}{n}(\nu_a n_{a1} \exp(-V_a/kT)$$
$$+ \nu_b n_{b1} \exp(-V_b/kT)) \qquad (35)$$

which, when substituted in (33), leads to the relation

$$p(n_{a1}, n_{a2}) = \frac{\nu_a n_{a1}f}{\nu_a n_{a1}f + \nu_b n_{b1}} \qquad (36)$$

that is of fundamental interest to us. The quantities ν_a, ν_b, and f appearing in this will generally be functions of both n_{a1} and n_{a2}. For simplicity we shall assume at the start that they are involved only through the combination

$$n_a = (n_{a1} + n_{a2})/2.$$

With the use of this form of $p(\xi, \eta)$ we readily find that when $\xi = \eta = n_a$

$$\frac{p(n_a)}{n_a} = \frac{\nu_a f}{\nu_a n_a f + \nu_b n_b},\tag{37}$$

$$\alpha = \frac{\nu_a \nu_b n f + \frac{1}{2}\nu_a \nu_b n_a n_b \dfrac{df}{dn_a} + \frac{1}{2} n_a n_b f(\nu_b \nu_a' - \nu_a \nu_b')}{(\nu_a n_a f + \nu_b n_b)^2}\tag{38}$$

$$\alpha - \beta = \frac{n \nu_a \nu_b f}{(\nu_a n_a f + \nu_b n_b)^2}.\tag{39}$$

Here ν_a' and ν_b' are the derivatives of ν_a and ν_b with respect to n_a. From (37) and (39) we readily find

$$\frac{D_c}{D_a{}^*} = \frac{\alpha - \beta}{p(n_a)/n_a} = \frac{n\nu_b}{(\nu_a n_a f + \nu_b n_b)}.\tag{40}$$

When f is very large, so that vacancies prefer to be near A atoms, the ratio (40) is $n\nu_b/\nu_a n_a f$. This is $2\nu_b/\nu_a f$ in the case in which $n_a = n/2$.

In the opposite case in which f is small, so that vacancies prefer B atoms, the ratio is n/n_b, which is 2 for 50–50 composition.

Similarly, we find that in the case of 50–50 composition

$$\frac{D_c}{D_a{}^* + D_b{}^*} = 2\frac{xy}{(x+y)^2},\tag{41}$$

in which

$$x = \nu_a n_a f, \quad y = \nu_b n_b.\tag{42}$$

This ratio attains the maximum value of $\frac{1}{2}$ when $x = y$. Thus in the case of the simple model which we have employed, D_c can never be larger than half the sum of the radioactive diffusion coefficients.

The results (38) and (39) are definitely dependent upon the simplifying assumptions made in determining α and β from $p(n_{a1}, n_{a2})$, as given by (36). If we assume that ν_a, ν_b, and f do not involve n_{a1} and n_{a2} merely through the quantity $n_a = (n_{a1} + n_{a2})/2$, we have in place of (39)

$$\alpha - \beta = \frac{n\nu_a \nu_b f + n_a n_b f \nu_b{}^2\left(\dfrac{\partial r}{\partial \xi} - \dfrac{\partial r}{\partial \eta}\right) + \nu_a \nu_b\left(\dfrac{\partial f}{\partial \xi} - \dfrac{\partial f}{\partial \eta}\right)}{(\nu_a n_a f + \nu_b n_b)^2},\tag{43}$$

where $r = \nu_a/\nu_b$.

As we have noted in the introduction, Johnson's experiments indicate that D_c is almost exactly equal to $D_a{}^* + D_b{}^*$. This result is not in accordance with the version of the foregoing model which leads to (41). On the other hand, it could arise from the extended version which leads to (43), provided the combinations of derivatives of r and f appearing in Eq. (43) are assumed to take the proper values. It is interesting to note that Johnson's results imply considerable inequality between the behavior of silver and gold atoms in the 50–50 alloy. This in turn suggests

that they should show[8] pronounced short-range order, even if long-range order is absent.

The writer is particularly indebted to Professor R. J. Maurer for several valuable discussions of this paper. Maurer was apparently the first to appreciate that the problems of chemical and radioactive diffusion are basically different if radioactive diffusion takes place in the absence of a chemical gradient.