Diffusion in Binary Alloys

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Darken has given a phenomenological theory of diffusion in binary alloys based on the assumption that each constituent diffuses independently relative to a fixed reference frame. It is shown that diffusion via vacant lattice sites leads to Darken's equations if it is assumed that the concentration of vacant sites is in thermal equilibrium. Grain boundaries and dislocations may act as sources and sinks for vacant sites and act to maintain equilibrium. The modifications required in the equations if the vacant sites are not in equilibrium are discussed.

I. INTRODUCTION

THERE has recently been much interest in diffusion in alloys from both an experimental and a theoretical standpoint. W. A. Johnson[1] has investigated the relation between diffusion of radioactive constituents of binary alloys of silver and gold and diffusion resulting from a gradient in the relative concentrations of the two metals. He finds that the chemical diffusion coefficient in an alloy in the 50–50 range of composition is larger than that of either of the constituents. Smigelskas and Kirkendall,[2] in a study of the migration of the boundary between 70–30 alpha-brass and copper as a result of diffusion, found that the diffusion is associated with a mass flow such as might be expected if zinc diffuses out of the brass more rapidly than copper diffuses in.

The theory of diffusion in alloys has been discussed recently by a number of authors from different points of view and apparently with differing results. Birchenall and Mehl[3] emphasize the role of the gradient of chemical potential as the motivating force in diffusion. Fisher, Hollomon, and Turnbull[4] treat the problem on the basis of the absolute theory of reaction rates, and consider diffusion via vacant lattice sites as well as by interstitial atoms. L. S. Darken[5] has developed the theory of diffusion in binary alloys from a phenomological standpoint. He assumes that each constituent diffuses independently of the other. F. Seitz[6] treated the vacancy mechanism of diffusion from the standpoint of kinetic theory. The purpose of the present note is to point out the connection between these various treatments, and in particular to show that the vacancy mechanism leads to Darken's equations if it is assumed that the concentration of vacant sites is maintained in local thermal equilibrium.

The method of calculation which we use is similar to that of Seitz. From a consideration of the effect on

rate of flow of terms in the free energy arising of non-ideality of the solid solution, we are led to equations for diffusion rates which are essentially the same as those of Fisher, Hollomon, and Turnbull. These equations involve the concentration of vacant lattice sites. Darken's equations then follow if it is assumed that the vacant sites are maintained in thermal equilibrium.

In Part II we give a brief description of Darken's theory. This is followed in Part III by a discussion of the thermodynamics of a binary alloy with vacant lattice sites. Part IV gives the theory of diffusion based on a model similar to that of Seitz.

II. DARKEN'S THEORY

Darken assumes that each constituent diffuses independently of the other so that, in a binary alloy with constituents A and B in concentrations N_A and N_B, the currents of atoms of the two types relative to some fixed reference frame are:

$$i_A = -D_A(\partial N_A/\partial x); \quad i_B = -D_B(\partial N_B/\partial x). \quad (1)$$

Although Darken does not wish to be as specific, we will assume that the reference frame is the crystal lattice. Since

$$(\partial N_A/\partial x) = -(\partial N_B/\partial x), \quad (2)$$

the total flow of atoms across a plane fixed in the lattice is:

$$i_A + i_B = -(D_A - D_B)(\partial N_A/\partial x). \quad (3)$$

Relative to a moving reference frame for which this flow vanishes, the flow of A atoms is

$$i_A - f_A(i_A + i_B) = -(f_B D_A + f_A D_B)(\partial N_A/\partial x), \quad (4)$$

where f_A and f_B are the fractional concentrations:

$$f_A = N_A/(N_A + N_B), \quad f_B = N_B/(N_A + N_B). \quad (5)$$

The factor

$$D_c = f_B D_A + f_A D_B \quad (6)$$

is the chemical diffusion coefficient as measured by the usual methods.

If there is a gradient of the concentration, $N_A{}^*$, of a radioactive tracer, the flow of radioactive atoms in an alloy in which the total concentration of A atoms is

[1] W. A. Johnson, Trans. A.I.M.E. 147, 331 (1942).
[2] A. D. Smigelskas and E. O. Kirkendall, Trans. A.I.M.E. 171, 130 (1947).
[3] C. E. Birchenall and R. F. Mehl, Trans. A.I.M.E. 171, 143 (1947), and subsequent discussion.
[4] Fisher, Hollomon, and Turnbull, Metals Tech. Tech. Paper 2344 (February, 1948).
[5] L. S. Darken, Metals Tech. Tech. Paper 2311 (1948).
[6] Frederick Seitz, Phys. Rev. 74, 1513 (1948).

uniform is

$$i_A{}^* = -D_A{}^*(\partial N_A{}^*/\partial x). \tag{7}$$

Darken attributes differences between D_A and $D_A{}^*$ to terms in the chemical potential other than those resulting from the entropy of mixing. It is the gradient of the chemical potential, μ_A, which is responsible for diffusion.

If in place of (2) or (7) we write

$$i_A = -C_A N_A \partial\mu_A/\partial x_A, \tag{8}$$

then C_A is the same for both chemical and radioactive diffusion. The chemical potential in the radioactive case involves only the entropy of mixing, so that, as for an ideal solution,

$$\mu_A{}^* = kT \log N_A{}^*. \tag{9}$$

Inserting (9) into (8) and comparing the result with (7), we find that

$$C_A = D_A{}^*/kT_A. \tag{10}$$

Comparing (8) and (2) for the case of chemical diffusion, we find the relation between D_A and $D_A{}^*$ which was used by Darken:

$$D_A = D_A{}^*(d(\mu_A/kT)/d \log N_A). \tag{11}$$

For an ideal solution D_A and $D_A{}^*$ are equal. In general, D_A may be either larger or smaller than $D_A{}^*$.

Similar equations apply to i_B. Darken points out that the thermodynamic equations of the alloy system,

$$d(\mu_A/kT)/d \log N_A = d(\mu_B/kT)/d \log N_B, \tag{12}$$

imply that

$$D_A/D_B = D_A{}^*/D_B{}^*. \tag{13}$$

Using values of μ_A from electrochemical data for the silver gold alloy Darken computed the value of the chemical diffusion coefficient, D_c, from the radioactive coefficients and found reasonable agreement with Johnson's measurements. Darken, of course, attributes a mass flow such as that found by Smigelskas and Kirkenall to a difference between D_A and D_B.

III. THERMODYNAMICS OF ALLOY WITH VACANT SITES

We suppose that of a total number of N sites, N_A are occupied by A atoms, N_B by B atoms, and N_v are vacant, so that

$$N = N_A + N_B + N_v. \tag{14}$$

We suppose that N_v is small compared with N_A and N_B. The Gibbs free energy may be expressed in the form:[7]

$$G = W(N_A, N_B, N_v) - kT(N \log N - N_A \log N_A$$
$$- N_B \log N_B - N_v \log N_v), \tag{15}$$

where the second term comes from the entropy of mixing and the first from all other causes. The chemical

potentials μ_A, μ_B, and μ_v are defined by equations of the form:

$$\mu_A = \partial G/\partial N_A = W/\partial N_A + kT \log f_A, \tag{16}$$

where f_A is the fractional concentration. In terms of the chemical potentials,

$$G = N_A \mu_A + N_B \mu_B + N_v \mu_v. \tag{17}$$

The potential μ_v is the free energy required to take an atom from the interior to the surface, forming an additional vacant site and increasing the total number of sites by one. If the vacant sites are in thermal equilibrium, $\mu_v = 0$. We do not assume this necessarily to be the case. In general,

$$\mu_v = kT \log(N_v/N_{ve}), \tag{18}$$

where N_v is the actual concentration of vacant sites and N_{ve} is the equilibrium concentration. In writing Eq. (18) we have assumed that $\partial W/\partial N_v$ is independent of N_v, as will be the case for small concentrations of vacancies. Equation (12) follows directly from Eq. (17) if it is assumed that $\mu_v = 0$, but is not strictly valid in the general case. Deviations from Eq. (12) will be small if the fractional concentration of vacant sites is small compared with unity or departs but little from equilibrium.

IV. DIFFUSION VIA VACANT SITES

We first discuss radioactive diffusion and then show how chemical diffusion is related to it. We assume, following Seitz,[6] that diffusion of both A and B atoms occurs by motion of atoms into neighboring vacant sites. For simplicity, we assume that the atomic volume is independent of concentration.

Consider two neighboring crystallographic planes 1 and 2, which are normal to the x axis and which are separated by a distance λ. We suppose that there is a gradient in the concentration, $N_A{}^*$, of tracer atoms in an otherwise uniform alloy, so that the number per unit area on plane 1 is $\lambda N_A{}^*$ and on plane 2 is $\lambda(N_A{}^* + \lambda(\partial N_A{}^*/\partial x))$. The concentration of vacant sites is assumed to be uniform. The rate at which A^* atoms go from plane 1 to plane 2 is then:

$$k_A \lambda N_v N_A{}^*, \tag{19}$$

and from plane 2 to plane 1,

$$k_A \lambda N_v (N_A{}^* + \lambda(\partial N_A{}^*/\partial x)), \tag{20}$$

where k_A is proportional to the rate at which an A atom jumps into a neighboring vacant site. Expressions (19) and (20) are based on the assumption that the concentration of A atoms which have vacant sites as neighbors in the adjacent plane is proportional to the average concentration of A atoms in the given plane.[8] The net

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[7] See, for example, M. W. Zemansky, *Heat and Thermodynamics* (McGraw-Hill Book Company, Inc., New York, 1943), p. 323.

[8] Dr. C. Herring has pointed out to the author that this assumption may not be valid. Consider the different ways in which a vacant site on the plane at $x+\lambda$ becomes adjacent to an A atom on the plane at x so that a forward jump of the A atom can take

flow of A^* atoms is the difference between (19) and (20)

$$i_A^* = -k_A\lambda^2 N_v(\partial N_A^*/\partial x), \qquad (21)$$

giving for the radioactive diffusion coefficient:

$$D_A^* = k_A\lambda^2 N_v. \qquad (22)$$

We next consider the case of chemical diffusion and assume a gradient in the concentration of vacant sites as well as of A and B atoms. The rate at which A atoms go from plane 1 to plane 2 is

$$k_f\lambda N_A(N_v+\lambda(\partial N_v/\partial x)) \qquad (23)$$

and from plane 2 to plane 1

$$k_b\lambda N_v(N_A+\lambda(\partial N_A/\partial x)), \qquad (24)$$

in which k_f and k_b are proportional to the frequency of jumps in the forward and backward directions, respectively. If, as a result of the concentration gradient in a non-ideal solution, the free energy of an A atom on plane 1 is slightly different from that of one on plane 2, the potential barrier over which diffusion takes place will not be symmetric, k_f will differ from k_b by terms of the order λ, and both will differ from k_A by terms of the same order.

The net rate of flow of A atoms is the difference between (23) and (24)

$$i_A = k_A\lambda^2\left(N_A\frac{\partial N_v}{\partial x}-N_v\frac{\partial N_A}{\partial x}\right)+(k_f-k_b)\lambda N_A N_v, \quad (25)$$

in which we have neglected higher order terms in λ. If ΔW is the change in free energy arising from non-ideality in the forward jump of an A atom,[9]

$$k_f/k_b = \exp(-\Delta W/kT)\simeq\left(1-\frac{\Delta W}{kT}\right). \qquad (26)$$

The effective height of the barrier impeding diffusion is increased for a forward jump and decreased for a reverse jump, and the difference in effective heights in

the two directions is ΔW. To a sufficient approximation,

$$k_f-k_b = k_A\Delta W/kT. \qquad (27)$$

An expression for ΔW may be obtained as follows. In a forward jump, the number of A atoms on the plane at $x+\lambda$ is increased by one and the number of vacant sites is decreased by one. On the plane at x the opposite changes occur. Thus to terms of the order λ

$$\Delta W=\left(\frac{\partial W}{\partial N_A}-\frac{\partial W}{\partial N_v}\right)_{x+\lambda}-\left(\frac{\partial W}{\partial N_A}-\frac{\partial W}{\partial N_v}\right)_x$$

$$=\lambda\frac{\partial}{\partial x}\left(\frac{\partial W}{\partial N_A}-\frac{\partial W}{\partial N_v}\right). \qquad (28)$$

Using (27) and (28) in (25), we find

$$i_A = k_A\lambda^2 N_A N_v\frac{\partial}{\partial x}\left[\log N_v-\log N_A\right.$$

$$\left.-\frac{1}{kT}\left(\frac{\partial W}{\partial N_A}-\frac{\partial W}{\partial N_v}\right)\right], \qquad (29)$$

which may be written in the form:

$$i_A = -C_A N_A\partial(\mu_A-\mu_v)/\partial x, \qquad (30)$$

where

$$C_A = k_A\lambda^2 N_v/kT = D_A^*/kT. \qquad (31)$$

Equation (29) is essentially the same as Eq. (27) of Fisher, Hollomon, and Turnbull.

Equation (30) is the same as Eq. (8) if $\mu_v=0$. Thus the mechanism of diffusion via vacant sites leads to Darken's phenomenological equations if the vacant sites are in local thermal equilibrium. No gradient of vacant sites is to be expected in the case of diffusion of a radioactive tracer. In chemical diffusion, where there is a vacancy current, grain boundaries and to a less extent dislocations will act as sources and sinks for vacant sites to help maintain local equilibrium. The associated plastic flow tends to keep the density of atoms constant.

If the concentration of vacant sites is not in thermal equilibrium, the more general Eq. (30), which is analogous to those of Seitz and of Fisher, Hollomon, and Turnbull, must be used. With use of Eq. (18) for μ_v, (30) includes a term in the concentration gradient of vacant sites. This could be transformed, following Seitz, to a term involving the current of vacant sites.

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place. One of the ways is that in which a reverse jump has just taken place, an A atom on $x+\lambda$ going to the plane at x. The number of these which will occur will depend in part on the concentration of A atoms at $x+\lambda$ instead of x. In the extreme case in which motion can take place only along strings of atoms parallel to the concentration gradient, a flow of vacant sites could take place without any associated diffusion. According to Dr. Herring's calculations, the error made in calculating the radioactive diffusion coefficient in a cubic monatomic substance by the above method is about 10 percent.

[9] See S. Glasstone, H. J. Laidlen, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), p. 530.