

# LATTICE DIFFUSION IN FACE-CENTRED CUBIC METALS

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## Abstract

The paper attempts to survey available information on lattice diffusion between two face-centred cubic metals. The Grube and Matano methods of determining diffusion constant are described. Various mechanisms of diffusion are outlined and the preference for the vacancy mechanism in the face-centred cubic metals, as judged from theoretically calculated values for activation energies, is discussed. The Kirkendall effect and the phenomenological equations of Darken, which take this effect in account, are stated. The Onsager equations for irreversible processes and their application to diffusion are mentioned. Reference is made to metallurgical processes involving diffusion phenomenon.

**D**IFFUSION is defined as the macroscopic transference of matter which tends to establish conditions of statistical equilibrium in the system. It follows the path of least resistance and can proceed by three distinct routes in a solid: (1) via lattice, (2) via grain-boundary, and (3) via surface. Lattice diffusion may, again, be divided into three types: (a) diffusion in interstitial alloys, (b) diffusion in loose-packed metals, and (c) diffusion in closed-packed metals. Lattice diffusion caused by a gradient in thermodynamic activity and occurring in a face-centred cubic metal forms the subject of this paper.

## The Usual Procedure of Determining Diffusivity: Fick's Laws: Their Limitations

The usual procedure of studying diffusion of a metal is to prepare a welded or electroplated couple, the two components of which contain different concentrations of the solute

whose diffusion constant is to be determined. Such a couple is held for a certain period of time at the temperature of study. After the diffusion has taken place for a specified time, thin layers are removed from the couple and analysed with respect to the solute. A curve of concentration versus distance from the initial interface, called the concentration-penetration curve, is then plotted. Fig. 1 shows such a curve, in which  $c$  is the concentration at any point in the diffusion zone and  $c_0$  is the final concentration, both values being measured over the initial concentration.

Two methods are available for the calculation of diffusivity from such curves. The first method, due to Grube, is used in cases where the diffusivity does not change with composition or where the difference in solute concentration in the two components of the couple is small. In the latter case, Grube's method gives the average value of diffusivity. The second method, due to Matano, is used in cases where the diffusivity changes with concentration. The variation of diffusivity with concentration is shown by the curved

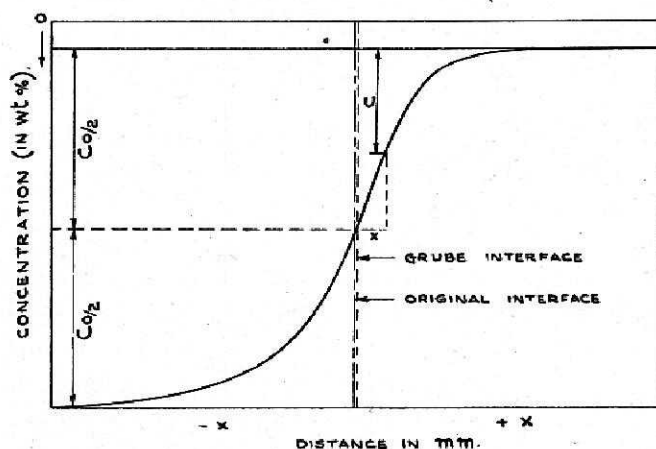


FIG. 1

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line when the  $c/c_0$  versus distance curve is plotted on probability paper<sup>1</sup>, as in Fig. 2. When the diffusivity does not change with concentration, the data follow a straight line. If probability paper is not available, the data are plotted in the following manner<sup>2</sup>. The distances are marked off linearly on the abscissa. The values of  $y$  satisfying the relation

$$2c/c_0 = 1 - \phi(y) \dots \dots \dots (1)$$

where  $\phi$  is the Gauss error function, are obtained from tables of Gauss error function, for several values of  $c/c_0$ , ranging from 0 to 1. Each value of  $y$ , obtained in this fashion, is marked off on the ordinate and labelled with the corresponding  $c/c_0$  value.

Grube's method depends upon Fick's second law of diffusion written in the form

$$\delta c/\delta t = D\delta^2 c/\delta x^2 \dots \dots \dots (2)$$

where  $t$  = time of diffusion,  $x$  = the distance from the interface, and  $D$  = diffusivity or diffusion constant.

The solution of this equation for diffusion across a plane of unit area, placed perpendicular to the direction of diffusion, when the composition of the two ends of the couple in the direction of diffusion remains constant, is<sup>3</sup>

$$\frac{c_0/2 - c}{c_0/2} = \phi(x/2\sqrt{Dt}) \dots \dots \dots (3)$$

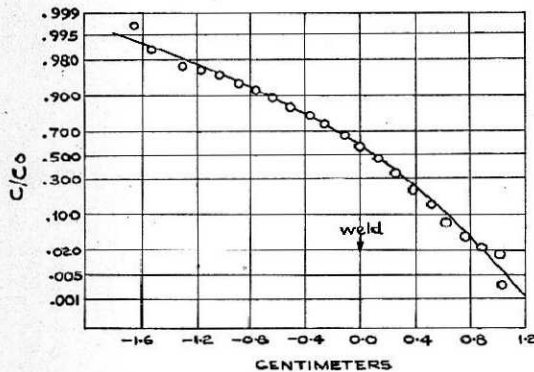


FIG. 2

For calculating the diffusivity by the Grube method a concentration-penetration curve is plotted.

Grube's interface is then drawn at 50-50 composition of the solute, as in Fig. 1, and the value  $x$  is measured from this interface. The value on the left-hand side of equation (3) is known and so the value of the expression within brackets on the right-hand side of the equation can be found out by consulting tables of Gauss error function. This value from the tables is equated to  $x/2\sqrt{Dt}$  and, since  $x$  and  $t$  are known,  $D$  can be calculated.

Fick's second law of diffusion for non-steady state is derived from his first law of diffusion for steady state. Fick's first law of diffusion can be expressed as

$$J = -D\delta c/\delta x \dots \dots \dots (4)$$

where  $J$  = flux or amount of material passing per unit time through unit area of a plane placed at right angles to the direction of diffusion.

Differentiating equation (4) with respect to  $x$ , and noting that  $\delta J/\delta x = -\delta c/\delta t$ , the second Fick's law of diffusion, for the case where  $D$  does not change with concentration, is obtained:

$$-\delta J/\delta x = \delta c/\delta t = D\delta^2 c/\delta x^2 \dots \dots \dots (5)$$

For the case where  $D$  changes with concentration, Fick's second law of diffusion takes the form

$$-\delta J/\delta x = \delta c/\delta t = \frac{\delta}{\delta x} (D\delta c/\delta x) \dots \dots \dots (6)$$

The second method of computing diffusivity by Matano's method depends upon Fick's second law of diffusion, stated in the form of equation (6). Boltzmann<sup>4</sup> first showed the method of solving this equation by using the relation

$$\lambda = x/\sqrt{t} \dots \dots \dots (7)$$

where  $\lambda$  is a variable. This relation was later derived empirically by Matano<sup>5</sup>.

The method of computing  $D$  by Matano's method is as follows. A curve of concentration (in atom per cent) versus penetration (in mm.) is drawn as in Fig 3. The Matano interface is then drawn by trial and error in such a manner that the areas ABC and ADE become equal. At any point M on the curve a tangent is drawn. Its slope is determined in cm. per cent. The area MFBC is measured in cm. per cent. The factor  $1/2t$ , where  $t$  = time of diffusion in days, is calculated. The diffusivity,  $D$ , in  $\text{cm.}^2$  per day is then given by the equation

$$D = \text{area MFBC} \times \text{slope of the tangent} \times \frac{1}{2}t \quad (8)$$

The limitations of Fick's second law may be mentioned here. The value of  $x$  becomes ambiguous when volume changes occur during diffusion<sup>6</sup>. This limitation may, however, be removed by introducing a modified measure of distance in place of  $x$ . If diffusion occurs through vacant sites, as in the case of f.c.c. metals, their concentration may differ from the equilibrium value. In such a case the validity of Fick's second law is limited to only low concentration gradients. Finally, Fick's second law fails if, during the diffusion process, lattice imperfections such as holes or dislocations are created<sup>7</sup>. In such cases the value of  $D$  will change with time. The benefits of using incremental couples with small initial differences in concentration have been emphasized in the above cases by Cohen, Wagner and Reynolds<sup>8</sup>.

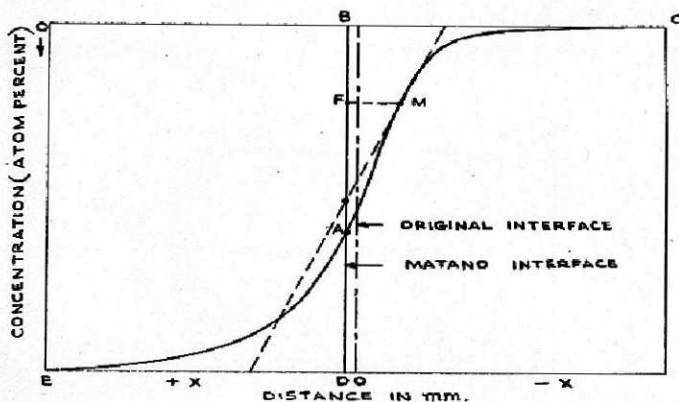


FIG. 3

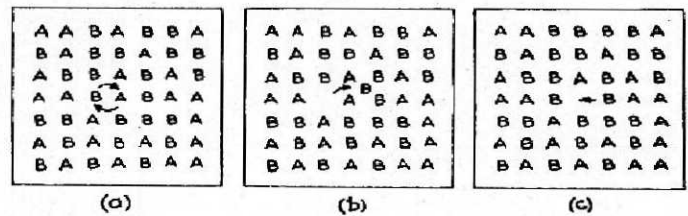


FIG. 4

### Mechanisms of Diffusion

Diffusion in solids may be described in terms of the three basic mechanisms illustrated in Fig. 4<sup>9,10</sup>. The exchange mechanism of diffusion is shown in Fig. 4(a); A squeezes through the lattice to the position of B, and B moves to occupy the position of A. In Fig. 4(b), a B atom leaves its normal position and enters into interstitial region. Such an atom may occupy a vacant lattice site or push a normal atom into interstitial position and take its place. In the latter case the displaced atom may push out another normal atom into interstitial position and may occupy its place; and when such a process is repeated, the interstitial distortion moves in the lattice in the form of a wave. Seitz<sup>11</sup> has called this particular mechanism of diffusion 'interstitialcy'. Where the B atoms are so small that they normally occupy interstitial positions between A atoms, then diffusion occurs by the migration of B atoms, the A atoms remaining stationary. Fig. 4(c) illustrates the third mechanism by which diffusion may occur when vacant lattice sites are already present in the crystal. Diffusion occurs by the occupation of a vacant lattice site by a B atom and the movement of this vacancy in the opposite direction.

Seitz<sup>12</sup> has pointed out that diffusion may be faster if two vacancies form a pair instead of remaining separately. In the former case, an atom can exchange place with either of the two vacancies more easily on account of a lower closed shell interaction.

Another model of vacancy diffusion in which the vacant sites associate preferentially with solute atoms has been discussed by Johnson<sup>13</sup>. This mechanism has a lower



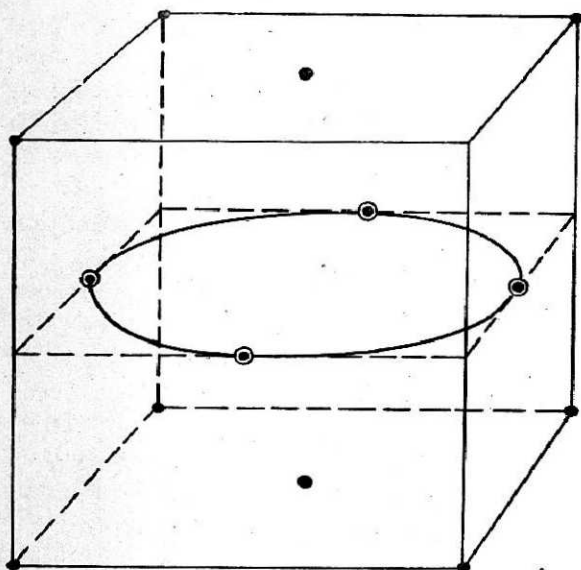


FIG. 5(a)

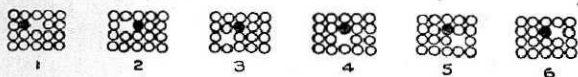


FIG. 5(b)

energy of activation than that in which an atom exchanges position with a vacancy. Johnson's model is illustrated in Fig. 5(a).

The ring mechanism of diffusion proposed by Zener<sup>14</sup> is actually a generalization of the first mechanism discussed above. Fig. 5(b) shows the four-ring mechanism of diffusion. The exchange mechanism, as can be seen, is a particular case of ring diffusion in which two atoms take part.

The 'crowdion' mechanism, proposed by Paneth<sup>15</sup>, is a variation of the interstitialcy mechanism; it differs from the latter only in the number of atoms over which the distortion is distributed.

#### Energy of Activation for Various Mechanisms

A comparison of calculated activation energies for various mechanisms for self-diffusion is shown in Table 1. Though sodium is a body-centred cubic metal, it is included to give an idea of the activa-

tion energy for the crowdion mechanism of diffusion.

TABLE 1

METAL	MECHANISM	THEORETICAL ACTIVATION ENERGY
Copper <sup>16</sup>	Exchange	240 K. cal./mole
Copper <sup>17</sup>	Interstitialcy	230 K. cal./mole
Copper <sup>18</sup>	Vacancy	64 K. cal./mole
Copper <sup>14</sup>	Ring	About 90 K. cal./mole
Sodium <sup>15</sup>	Crowdion	About 14 K. cal./mole

The experimentally observed value of activation energy for self-diffusion in copper is 48 K. cal./mole<sup>19</sup>; therefore, the vacancy mechanism of diffusion seems to be the most probable for copper. Huntington and Seitz's<sup>16</sup> calculations show that similar considerations will apply to all close-packed lattices.

#### Kirkendall Effect

The important phenomenon in diffusion, namely the Kirkendall effect, will now be described. In 1946, Smigelskas and Kirkendall<sup>20</sup> placed thin molybdenum wires at the copper-brass interface of their diffusion couple (see FIG. 6) and observed that the wires on opposite faces have moved towards one another after the diffusion anneal.

Since then, Kirkendall effect has been observed in many other single-phase inter-diffusing systems such as Cu-Ni<sup>21-24</sup>, Cu-Au<sup>21</sup>, Ag-Au<sup>21,23,24</sup>, Ag-Pd<sup>23,24</sup>, Ni-Co<sup>23,24</sup>, Ni-Au<sup>23,24</sup>

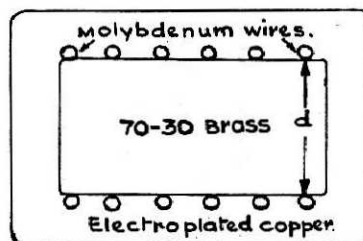


FIG. 6

and Fe-Ni<sup>24</sup> and in the  $\alpha$ -range of Al-Cu<sup>21,25</sup>. These experiments indicate the very high probability of the occurrence of Kirkendall effect in all the f.c.c. metals during inter-diffusion. When the markers are placed at the initial interface, the extent of marker shift is observed to be proportional to the square root of diffusion time. The marker shift increases with rising temperatures for the same annealing period and is larger the greater is the initial difference in composition of the two halves of the couple. In all cases, the movement of the markers is towards the component having the lower melting point.

The Kirkendall effect implies that, relative to the fixed lattice or moving markers, one element is diffusing more rapidly than the other. For example, in the copper-brass couple the number of zinc atoms crossing the inert markers from the brass towards copper side is greater than the number of copper atoms crossing the markers from the opposite direction. The markers, by their movement towards the brass side, allow the zinc atoms to be accommodated in the copper side and, at the same time, permit the zinc-losing brass to shrink.

The shifting of the markers indicates that diffusion in common face-centred metals does not occur by exchange or Zener's ring mechanism because these mechanisms cannot cause a marker shift. Both the vacancy and interstitial mechanisms can cause such a shift and this shifting may be explained in either of the following two ways.

(1) Zinc atoms diffuse into copper interstitially and occupy normal lattice positions there. The resulting expansion in copper compensates exactly for the contraction in brass so that constant atomic density is maintained.

The calculations of Huntington and Seitz<sup>16</sup> indicate that this process of diffusion is highly unlikely.

(2) If it is assumed that the vacancies exchange with zinc atoms more readily, the flow of zinc atoms, arising because of con-

centration gradient, will cause a shifting of markers towards the brass side; at the same time vacancies are pumped from the copper-rich side into brass. These vacancies, if there are suitable vacancy sinks, may be totally obliterated.

Besides the suitable energy of activation that the vacancy mechanism possesses, the occurrence of porosity in diffusion zone indicates that this mechanism is adequate to describe diffusion in the f.c.c. metals.

The vacancy mechanism, however, needs sources and sinks for vacancy and Seitz<sup>26</sup> suggested that the external surface acts as the source of vacancies. Since Kirkendall effect has not been found to depend on volume and on whether the outer surface is of brass or copper, the surface cannot act as a source of vacancies for diffusion. Nabarro<sup>27</sup> has shown that dislocations can act as sources and sinks for vacancies.

### The Phenomenological Equations of Darken: Some Features of Diffusion

The Kirkendall effect, it has been pointed out earlier, implies that the two diffusing constituents in a binary system inter-diffuse at different rates across the fixed lattice. It is, therefore, necessary to have two diffusion constants,  $D_a$  and  $D_b$ , for the two constituents, a and b, to account for diffusion relative to the fixed lattice. Darken<sup>28</sup> has shown that the usual diffusivity,  $D$ , as determined by Matano's method, is related to the two diffusivities  $D_a$  and  $D_b$  by the equation

$$D = N_a D_b + N_b D_a \dots \dots \dots (9)$$

where  $N_a$  and  $N_b$  are the fractional concentrations of the constituents a and b. He has also shown that planes of the lattice or markers at points in diffusion zone where the concentration gradient is  $\delta N_a / \delta x$  move relative to the planes where there is no concentration gradient with a velocity  $v$ , given by

$$v = (D_a - D_b) \delta N_a / \delta x \dots \dots \dots (10)$$

When the markers are placed at a position where no concentration changes occur, a condition approximately fulfilled by the markers at the initial join,  $x$  is proportional to  $t^{\frac{1}{2}}$  and  $v$  is given by  $x/2t$ . Knowing  $D$  and  $v$ , it is possible to solve equations (9) and (10) simultaneously, to give the values of  $D_a$  and  $D_b$ .

For the correct appraisal of Darken's equations it is necessary to examine the assumptions made in their derivation, which are that (1) changes in lattice parameter can be ignored during diffusion, (2) a non-defective lattice results after diffusion on account of co-ordinated shrinkage and expansion, (3) the shrinkage occurs only in the direction of diffusion so that a constant cross-section is maintained through which diffusion occurs, and (4) the vacancies are maintained in thermodynamic equilibrium<sup>29</sup>. The first assumption may be avoided by measuring distances in terms of lattice spacings instead of centimeters<sup>30</sup>. Experimentally, the second assumption has not been found to be true in all cases. Porosity is always found in the diffusion zone of the component suffering a net loss of atoms and giving rise to an increase in the overall length of the couple. Porosity increases with increasing time of diffusion and is greater the larger is the initial difference in concentration. As regards the third assumption, Seith and Kottmann<sup>23</sup> have found that expansion and contraction occur on the free surface of the couple in a direction perpendicular to that of diffusion. The swelling occurs in the part which receives a net flux of atoms and the contraction in that part which suffers a net loss of atoms (see FIG. 7).

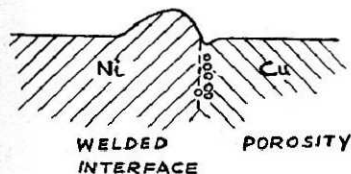


FIG. 7

Marked porosity in some specimens suggests that the fourth assumption is also not valid.

The factors discussed above also affect the value of  $v$ . Further,  $x$  is proportional to  $t^{\frac{1}{2}}$  only when the concentration does not change at the plane of markers. Seith and Kottmann<sup>24</sup> have shown that this relation does not apply when concentration changes occur at the marker plane, as is the case when they are placed in the diffusion zone at some distance from the initial join. In such cases the value of  $v$  must be obtained from several measurements of  $x$  and  $t$ .

Porosity and lateral dimensional changes are marked in cases where diffusion occurs in pure dissimilar metals; for diffusion between a metal and one of its alloys and when the concentration gradient is not large, these phenomena are less marked, and their effect on the measurement of  $D$  and  $v$  may be well within the range of experimental error<sup>31</sup>.

Another complicating feature in diffusion is the introduction of stresses in the lattice on account of the addition and removal of planes of atoms. These stresses can cause plastic flow. Sometimes recrystallization and grain growth<sup>32</sup> and polygonization<sup>22</sup> in the diffusion zone may be caused by these stresses.

On account of these complicating factors, Le Claire<sup>31</sup> points out that the rate of self-diffusion, which depends only upon the number of vacancies and upon the probability of exchange of atoms with vacancies, shall give the most fundamental quantity underlying all diffusion phenomena, namely the average number of random jumps made per second by each atom in a homogeneous alloy in thermodynamic equilibrium.

### Variation of $D$ with Temperature

The variation of  $D$  with temperature is usually expressed by the equation

$$D = D_0 e^{-Q/RT} \dots \dots (11)$$

where  $D_0$  is a constant,  $Q$  is the energy of activation,  $R$  is the gas constant and  $T$  is



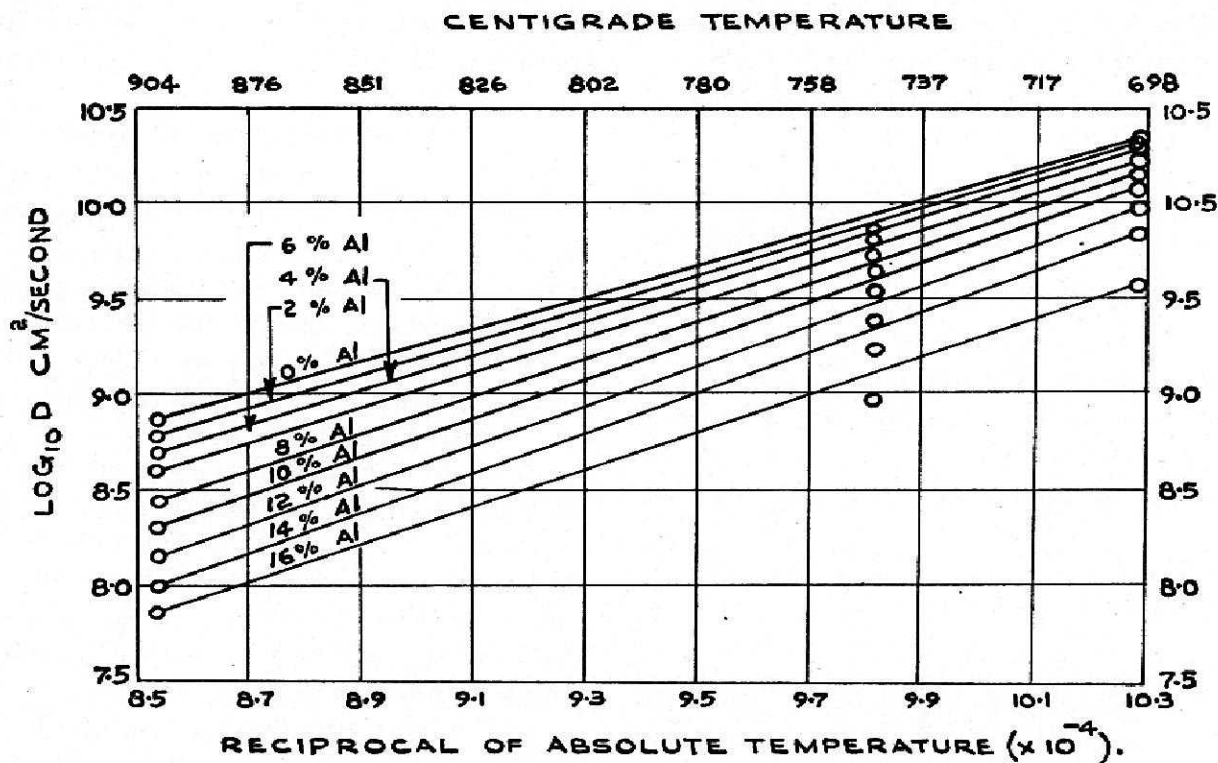


FIG. 8

the absolute temperature. On taking logarithms the equation becomes

$$\ln D = \ln D_0 - Q/RT \dots \dots (12)$$

It is clear that if  $\ln D$  is plotted against  $1/T$  (the values of  $D$  for one solute concentration being obtained at several temperatures), the slope of the straight line obtained equals  $Q/R$ . Fig. 8<sup>33</sup> shows the curves obtained by plotting  $\log D$  versus  $1/T$  for copper-aluminium alloys of different compositions. Since the lines for various concentrations of aluminium are not parallel, it is clear that  $Q$  varies with concentration. The manner in which  $Q$  varies with concentration for the copper-aluminium alloys mentioned above is shown in Fig. 9<sup>33</sup>.

Zener<sup>34</sup> has applied the theory of reaction rates for the most probable values of  $D_0$  and  $Q$  for gold, silver, lead and copper. His calculations also suggest that self-diffusion in these metals occurs by the vacancy mechanism.

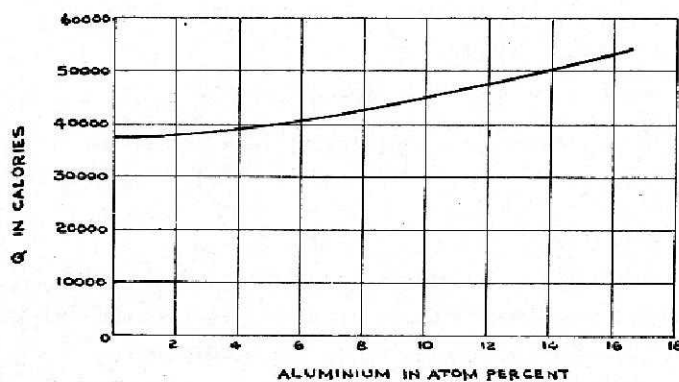


FIG. 9

### The Phenomenological Equations of Diffusion

If a solid contains more than one type of atoms, a flux of atomic species  $a$  may be induced by a gradient in the concentrations of atomic species  $b$ . Since activity is more fundamental than concentration, it is more precise to substitute activity for concentration

in the above statement. Mathematically<sup>29</sup>, for a system of  $n$  atomic species

$$J_i = - \sum_{j=1}^n M_{ij} (\delta\mu_j / \delta x) \dots \dots \dots (13)$$

where  $M_{ij}$ 's are the mobilities. From Onsager's<sup>35</sup> principle of microscopic reversibility

$$M_{ij} = M_{ji} \dots \dots \dots (14)$$

Equation (13) is applicable to all the three basic mechanisms of diffusion. If the lattice sites are conserved, then the net flux in a volume is zero, i.e.

$$\sum J_i = 0 \dots \dots \dots (15)$$

and equation (13) then becomes

$$J_i = - \sum_{j=1}^n M_{ij} \left\{ \frac{\delta(\mu_j - \mu_x)}{\delta x} \right\} \dots \dots (16)$$

If the vacancies are labelled as the  $n$ th constituent, and if they are maintained in equilibrium, equation (16) becomes

$$J_i = - \sum_{j=1}^{n-1} M_{ij} (\delta\mu_j / \delta x) \dots \dots \dots (17)$$

If the cross-terms are omitted from equation (17), then

$$J_i = - M_i \delta\mu_i / \delta x \dots \dots \dots (18)$$

This is the equation that has been used by Darken<sup>28</sup> in conjunction with the equation

$$J_i = - D_i \delta e_i / \delta x \dots \dots \dots (19)$$

defining  $D_i$ , for the derivation of  $D_a$  and  $D_b$ , the two diffusivities for the two constituents, when the marker shift is observed.

Darken's<sup>28</sup> equations are, therefore, a simplification of the more general equation (16), in which it is assumed that vacancies are in thermal equilibrium and that the cross-terms are zero. The assumption that vacancies are in equilibrium will be valid in the case of self-diffusion experiments and in chemical diffusion experiments, if there are sources and sinks for vacancy to maintain equilibrium. As regards the cross-terms, at least those representing coupling between the flow of vacancies and the flow of several atomic species should not be neglected since

there is such an intimate relation between them<sup>31</sup>.

### Practical Applications

The phenomenon of diffusion is intimately connected with most of the metallurgical processes. A cast metal, to begin with, is inhomogeneous and annealing treatments are designed to inter-diffuse the inhomogeneities. Different heat treatments such as carburizing, nitriding, aluminizing, sherardizing, etc., are dependent upon diffusion. The application of two metals at high temperature requires a study of their diffusion characteristics; 'cermet' for high temperature application is an example under reference. In the sintering of metal powders also, for the production of porous bearings, diffusion plays a leading role.

Studies on diffusion in the f.c.c. metals assume importance in relation to inhomogeneities encountered during casting, hot-working or welding of an alloy containing two-face-centred cubic metals. For example, the evaporation of zinc from the surface during hot-rolling of brass may cause a rush of zinc to the surface, leaving behind vacancies. This may be of importance particularly when the grain size of the sheet is large, since then the concentration of vacancies may be quite large. The process of calorizing and siliconizing also involves inter-diffusion between face-centred cubic metals. It is possible that surface imperfections may result during the process on account of the expansion of the higher melting point metal to accommodate the lower melting point diffusing metal. During the process of sintering of metal powders of f.c.c. metals also, the Kirkendall effect may play an important role.

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