

A Commentary on “Diffusion, Mobility and Their Interrelation through Free Energy in Binary Metallic Systems,” L.S. Darken: *Trans. AIME*, 1948, vol. 175, p. 184ff

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AS an undergraduate and graduate student of metallurgy, the subject of diffusion at first appeared to me as being rather empirical when compared with thermodynamics. It wasn't until the end of the course when multicomponent diffusion was discussed and when Darken's phenomenological equations were described that I appreciated the fundamental nature of diffusion and how the earlier descriptions of flux were really only special cases of Darken's description in his classic article. Indeed, now that I teach diffusion and transport myself, I often wonder whether the subject should be introduced through Darken's equations, which related diffusivity to mobility and activity, rather than through Fick's First Law.

In his classic article^[1] titled “Diffusion, Mobility and Their Interrelation Through Free Energy in Binary Metallic Systems,” Dr. Darken presents his phenomenological analysis of diffusion on binary systems. It is divided into two interrelated sections, with the first handling the issue of marker movement and the second handling the effect of nonideality on diffusion.

His treatment is general, but he utilizes the then recent experimental work by Smigelskas and Kirkendall,^[2] which showed marker movement in the Cu-brass couple as an example for the first part of his analysis. As a basis for his analysis, he separated the diffusive flux from the flux associated with marker movements (gross material flow) and established a Lagrangian reference frame from which both fluxes were observed. Then, by making a critical assumption that gram atomic volume (density) is constant, he developed two equations: $v = (D_2 - D_1) \frac{\partial N_2}{\partial x}$ and $D = N_1 D_2 + N_2 D_1$. The first expression identifies individual (intrinsic) diffusion coefficients for the two diffusing species and quantitatively links the marker movement to their difference and the concentration gradient at a given location. The significance of the equation is that, assuming that there are two different diffusivities and markers are found to move, it shows how the problem can be treated. The second equation

evolves from the first because the homogenization rate is dependent on the two diffusivities, which are linked through the marker movement. It essentially identifies the chemical diffusion coefficient that is measured through the Boltzmann–Matano analysis.^[3]

The work by Johnson^[4] shows that the diffusivity in the 0.5Au–0.5Ag system deviates significantly from what is expected from the ideal tracer diffusivity and is used as a basis for the second part of his analysis. This analysis is, in my opinion, possibly even more general in nature because it only assumes that a drift velocity on atoms results from the force arising from the magnitude of a potential gradient. The resulting equation, $D = (N_1 D_2^* + N_2 D_1^*) \left(1 + N_2 \frac{d \ln \gamma_2}{d N_2} \right)$, provides the invaluable link that describes how the chemical diffusion coefficient deviates from the ideal (tracer) coefficient, depending on the nature of the thermodynamic solution. Thus, the equation describes a dynamic phenomenon in terms of a thermodynamic state function in an elegant manner and describes how the interactions between the elements (or the enthalpy of mixing) influences diffusion, and how it could lead to uphill diffusion. In practice, this information provides a way to utilize databases and models on thermodynamic solutions to predict diffusion coefficients in non-ideal systems.

The beauty of Darken's analysis lies in that it is devoid of any assumptions of mechanisms or structural aspects of the material. Indeed, at the very onset of his introduction, he exemplifies dissimilar ion mobility in nonmetallic systems, such as Ag₂S and FeO, in addition to the classic Cu–Zn system used in the experiments of Smigelskas and Kirkendall.^[2]

It comes as no surprise that this article published in 1948 still rates as one of the most cited articles in our community. Beyond the elegance and scientific importance of Darken's article, it is of practical importance to processing and high-temperature performance of more or less all structural multicomponent alloys that contain substitutional alloying elements (e.g., alloy- and stainless steels and super-alloys). His treatment also has been extended to ceramics,^[5] polymers,^[6] metallic melts,^[7] and has been used in structurally very different systems, such as the molecular diffusion of CH₄ and CF₄ in Zeolite,^[8] which in effect confirms the generality of Dr. Darken's elegant analysis.

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Diffusion, Mobility and Their Interrelation through Free Energy in Binary Metallic Systems

BY L. S. DARKEN,* MEMBER AIME

(New York Meeting, February 1948)

It has been known for sometime that in an ionic lattice, such as that of Ag_2S or FeO , the migration velocity of the anion may differ markedly from that of the cation, the cation being usually the more mobile. It has been shown, for example, that during the formation of silver sulphide tarnish on silver, the tarnish layer grows principally by the motion of silver cations through an essentially stationary silver sulphide lattice. Similarly, the growth of wüstite scale on iron proceeds principally by motion of iron ions, this being accomplished with the aid of vacant iron lattice sites into which the iron may readily move. Likewise investigations of solid solutions of various salts show that there is usually considerable difference in the mobility of the different cations. Measurements of the mobility of various metals in liquid mercury indicate that the various metals move at different rates relative to the mercury.

In view of the foregoing it seems reasonable to suppose that when any single phase solution is acted upon by a field, the atoms of different elements respond in different ways; in particular, that the force arising from a particular concentration gradient in a binary alloy would cause the atoms of one component to move with a drift velocity which is in general different from that of the atoms of the other component. The recent experiments of Smigelskas and Kirkendall¹ support this viewpoint, since they found, in essence, that during diffusion in alpha brass

zinc moves appreciably faster than copper. This was evidenced by the relative motion of inert molybdenum wires. Such a phenomenon is incompatible with the place interchange theory of diffusion proposed by several authors, most recently by Birchenall and Mehl.² This theory has, however, also been questioned^{3,4} for other reasons, principally because of the high energy required for direct atomic interchange. The rather large difference between self-diffusivity, as determined by tracer technique, and mutual diffusivity, as determined with the aid of another element at low concentration, might also be interpreted as favoring the above idea; however, Birchenall and Mehl have pointed out that there is another possible interpretation of this difference; this is discussed later. A rather interesting and pertinent observation was made by Schwartz,⁵ who noticed that tungsten lamp filaments, heated by direct current, commonly fail by necking down in the region at the temperature gradient near the positive end, with a concomitant swelling at the corresponding position near the negative end. He introduces considerable auxiliary evidence to show that this phenomenon is occasioned by the motion of tungsten cations which migrate in the high temperature region from the positive end toward the negative end. The mechanism of this migration is not clearly understood. If, however, this experimental evidence be accepted, we are forced to conclude that alloying elements in the tungsten may migrate by the same or a similar mechanism, whatever it may be, at a greater or lesser rate, thus giving rise

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¹ References are at the end of the paper.

to a phenomenon similar to that observed by Smigelskas and Kirkendall in brass.

Since the mechanism (or mechanisms) of diffusion processes in metals is not established and the Boltzmann (or Matano) method is inadequate for the cases discussed above, there seems to be required a more general phenomenological treatment of the problem.

If displacement or motion of one component of a binary alloy is to be considered, then the first problem is to define this motion, in other words to decide how this displacement is to be measured and what is to be the criterion of displacement. This is primarily a problem of choice of coordinate axes for diffusion, and is very similar to the problem of determining the motion of water in a stream. The velocity of the water is measured by throwing into it a small chip of some material which will remain suspended therein. The velocity of the water in the vicinity of the chip is then taken as being the velocity of the chip. Use of a paddle wheel, or screw, is merely a variation of this fundamental technique. Objections can be made to this chip method; for example, a critic could maintain that the particular chip used might be equipped with motor and propeller, or that it was jet propelled by some chemical reaction. To meet such an objection it would be necessary to investigate for possible means of propulsion and try several chips of different composition and then determine whether all gave the same result under the same conditions. Having determined that such was the case, there would seem to be no alternative to accepting the velocity of the chip as that of the stream. In diffusion experiments carried on in such a stream, it would seem reasonable to choose coordinate axes which were at rest relative to the inert chips. If the stream velocity were not uniform so that chips moved relative to each other, then it would be necessary to devise some scheme whereby at each point diffusion was related to coordinate axes fixed relative to the chips

in the vicinity of that point. It would certainly be foreign to our accepted notion of diffusion to attribute any motion shared by the inert chips to a diffusion process. For example, if the stream flowed more rapidly on the right side than on the left and if, at some instant, salt were added at an upstream position and then samples were taken at a downstream position, it would undoubtedly be found at the downstream station that the salt content increased on the right side before it did on the left. One would hardly be tempted to conclude from this that the diffusivity of salt in water was greater on the right side of the stream than on the left.

Smigelskas' and Kirkendall's experiment serves as a rather pointed reminder that a very similar situation prevails in diffusion experiments in metals. Since the gross motion during diffusion is not as obvious as that of flowing water, the choice of coordinate axes in the past has not been based on any sound consideration but has been more a matter of convenience in mathematical treatment. In view of the somewhat improved nature of experimental data in this field and of the observations by Smigelskas and Kirkendall, it seems appropriate to attempt to settle this matter. Their method of using small inert wire markers to establish the origin of a coordinate system to which diffusion phenomena are to be referred seems an excellent choice, particularly since it involves no assumption whatsoever as to the mechanism of the diffusion process or as to the nature of the metallic state. It is as simple in principle as the chip method of measuring stream velocity and if there is any alternative method it is certainly not obvious. The objection that perhaps these particular markers are subject to some unknown force is answered by the fact that other markers, such as "ghost lines" and nonmetallic inclusions, move identically, similarly to the way chips of various materials move together in the stream of water. There would seem to remain the alternative of referring diffusion

phenomena to a set of coordinate axes fixed in the lattice. But a lattice point is unobservable and, if we adhere to the operational method, so strongly upheld by Bridgman, a concept for which there is no corresponding operation is meaningless; hence, this concept of a coordinate system fixed relative to unobservable lattice points seems, for the present, fruitless and devoid of meaning. Further, it is not known whether there exists a valid "law of conservation of lattice points." Even if these difficulties were overcome, there seems to be nothing to be gained by such a choice of axes, for if the statistical motion of copper atoms in brass, for example, were identical with the motion of inert molybdenum markers, one would hardly call this a diffusion of copper, even if both moved relative to the lattice.

The next part of this paper deals with unidimensional diffusion in the light of the above discussion. With the simplifying assumption that the total volume change is negligibly small it is shown that if a gross motion, as determined by relative motion of inert markers occurs, the phenomena may be completely represented by two simultaneous equations, one of which is identical with the usual "Matano solution." The final part deals with the application of free energy (activity and activity coefficients) to the results of the next section and includes an application to the silver-gold system.

A MORE GENERAL PHENOMENOLOGICAL TREATMENT OF THE UNIDIMENSIONAL DIFFUSION PROBLEM

Let us consider the unidimensional diffusion phenomena which take place when two thick, long rods, each initially a homogeneous alloy of the same two elements though in different proportion, are joined at a plane interface. The sides must be adequately protected so that all diffusion and motion occur parallel to the axis. Since it is desired to consider gross flow as well as diffu-

sion, let it be assumed that many sets of small inert markers (in principle, vanishingly small) are placed in the rods, each set perpendicular to the axis, so that the position of all points may be determined by section and examination at any arbitrary time. Only that motion which is relative to the markers is considered as directly attributable to diffusion.

In any very small region we set up a uniform distance axis, y , the origin of which is fixed relative to a marker. In this small region all changes of composition at a fixed place in this reference frame may properly be attributed to diffusion and it follows that D_1 , the diffusivity of component one, may be defined by the relation that the rate of passage of component one across a plane of unit area, fixed in the y coordinate system normal to the y axis, equals $-D_1 \frac{\partial C_1}{\partial y}$.

where C_1 is the concentration of component one, in atomic units per unit volume. Under the postulated condition that relative motion of the markers occurs, the above coordinate system is valid only for a very limited distance from its origin, since at greater distance the markers move in this coordinate system and the rate of passage of component one across a unit area is not attributable to diffusion only but is in part due to flow with the markers; consequently, this rate may not be equated to $-D_1 \frac{\partial C_1}{\partial y}$.

In order to avoid the use of an infinitude of coordinate systems to meet this situation, it may first be observed that a transformation from the y coordinate system to any other linear system, say an x distance axis, which is parallel to the y -axis but which may be in motion relative thereto, leaves the expression $-D_1 \frac{\partial C_1}{\partial y}$ unaltered except for the substitution of x for y ; thus it becomes $-D_1 \frac{\partial C_1}{\partial x}$ which is still the rate of passage of component one across a unit plane fixed relative to the inert markers.

The x -axis may now be used as a common reference axis for all points in the system. Relative to this x -axis the inert markers have a velocity, v , which is a function of position (x) and time (t). The rate of transport of component one across a unit plane normal to the x -axis and at some fixed point thereon may now be divided into two parts:

1. That by diffusion, or that which moves across a plane which is stationary relative to the local inert markers, which is $-D_1 \frac{\partial C_1}{\partial x}$; and 2. That by motion in common with the inert markers which is $C_1 v$. Thus the total rate of transport of component one across such a plane is $- \left[D_1 \frac{\partial C_1}{\partial x} - C_1 v \right]$. Equating the rate of

accumulation in any unit volume $\frac{\partial C_1}{\partial t}$ to the excess of the inflow over the outflow,

$$\frac{\partial}{\partial t} \left[D_1 \frac{\partial C_1}{\partial x} - C_1 v \right],$$

$$\frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x} \left[D_1 \frac{\partial C_1}{\partial x} - C_1 v \right] \quad \text{Eq 1}$$

A corresponding equation holds for component 2

$$\frac{\partial C_2}{\partial t} = \frac{\partial}{\partial x} \left[D_2 \frac{\partial C_2}{\partial x} - C_2 v \right] \quad \text{Eq 2}$$

Adding and inserting the relation that the total number of gram atoms per unit volume $C = C_1 + C_2$

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[D_1 \frac{\partial C_1}{\partial x} + D_2 \frac{\partial C_2}{\partial x} - C v \right] \quad \text{Eq 3}$$

On the simplifying assumption that the gram atomic volume, hence C , is constant,

$$\frac{\partial C}{\partial t} = 0 \text{ and Eq 3 reduces to}$$

$$\frac{\partial}{\partial x} \left[D_1 \frac{\partial C_1}{\partial x} + D_2 \frac{\partial C_2}{\partial x} - C v \right] = 0 \quad \text{Eq 3a}$$

which on integration becomes

$$D_1 \frac{\partial C_1}{\partial x} + D_2 \frac{\partial C_2}{\partial x} - C v = I \quad \text{Eq 3b}$$

where I is an integration constant. At very great distances, in either direction, from

the initial join, $\frac{\partial C_1}{\partial x}$ and $\frac{\partial C_2}{\partial x}$ are zero.

Hence $C v_\infty = I$ where v_∞ is the velocity of the inert markers at very great distances. It is now clear that the simplest choice of x axis is one rigidly fixed in the ends of the bar. Adopting this choice, $v_\infty = 0$ and $I = 0$. Then

$$v = \frac{I}{C} \left[D_1 \frac{\partial C_1}{\partial x} + D_2 \frac{\partial C_2}{\partial x} \right] \quad \text{Eq 4}$$

Inserting this value for v in Eq 1,

$$\frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x} \left[D_1 \frac{\partial C_1}{\partial x} - \frac{C_1}{C} D_1 \frac{\partial C_1}{\partial x} - \frac{C_1}{C} D_2 \frac{\partial C_2}{\partial x} \right] \quad \text{Eq 5}$$

Or in terms of the atom fraction $N_1 = \frac{C_1}{C}$

and $N_2 = \frac{C_2}{C}$, C being constant,

$$\frac{\partial N_1}{\partial t} = \frac{\partial}{\partial x} \left[(N_2 D_1 + N_1 D_2) \frac{\partial N_1}{\partial x} \right] \quad \text{Eq 5a}$$

Solving this equation in the usual manner, by making use of the variable $\lambda \equiv \frac{x}{t^{1/2}}$ and trying for solution $N_1 = f(\lambda)$, it reduces to:

$$-\frac{1}{2} \lambda dN_1 = d \left[(N_2 D_1 + N_1 D_2) \frac{dN_1}{d\lambda} \right]$$

As x and t have thus disappeared, it is proved that $N_1 = f(\lambda)$ is the solution of Eq 5A, providing the boundary conditions are satisfied; inspection shows that they are, the origin being selected at the initial position of the join. Integrating from a distant point where $N_1 = N_1^0$ to the one corresponding to composition N_1 :

$$N_2 D_1 + N_1 D_2 = \frac{-\frac{1}{2} \int_{N_1^0}^{N_1} \lambda dN_1}{dN_1/d\lambda} \quad \text{Eq 6}$$

In the past the diffusivity designated D was found as a function of concentration by the Matano,⁶ or Boltzman,⁷ method and D as actually determined and recorded was

identical with the expression on the right of Eq 6.* Hence

$$D = N_2 D_1 + N_1 D_2 \quad \text{Eq 7}$$

The diffusivities as recorded in the literature are therefore correct in principle, but incomplete in the sense that at any particular concentration D_1 and D_2 cannot be evaluated from D alone. The evaluation of D_1 and D_2 requires another relation in addition to Eq 7. This is conveniently taken as Eq 4 rewritten in terms of atom fractions

$$v = (D_2 - D_1) \frac{\partial N_2}{\partial x} \text{ or}$$

$$v = (D_1 - D_2) \frac{\partial N_1}{\partial x} \quad \text{Eq 8}$$

These two Eq 6 and 8 (or 7 and 8) may be regarded as completely descriptive of isothermal linear diffusion in a single phase composed initially of two uniform substances during which the atomic volume remains constant.† This assumption also implies the constancy of the total volume; it is local volume changes that are considered.

Determination of v . With the aid of the above equations, D_1 and D_2 may be found from the usual type of data leading to the evaluation of D plus a knowledge of the velocity of the inert markers. As this latter requires in general the use of several specimens in order to plot position versus time it seems desirable to establish the behavior of such inert markers insofar as possible in order to minimize the amount of experi-

* That this proof be complete it is necessary to show that the choice of origin is the same in the two cases. This may be done as follows: The material that disappears from one side of any plane (moving or stationary) parallel to the original join, must appear on the other. In particular this is true of the stationary plane initially at the join. Hence $\int_{x=+\infty}^0 x dN_1 = \int_{x=-\infty}^0 x dN_1$. As this expression also defines the "Matano interface" the proof of Eq 7 is completed.

† D_1 and D_2 may be found explicitly by simultaneous solution of Eq 6 and 8.

$$D_1 = \frac{\partial}{\partial N_1} \left[N_1 v - \frac{1}{2t} \int_{N_1^0}^{N_1} x dN_1 \right]$$

$$D_2 = \frac{\partial}{\partial N_2} \left[N_2 v - \frac{1}{2t} \int_{N_2^0}^{N_2} x dN_2 \right]$$

mental data required. This may be done easily for an inert marker initially at the join. From the fact that the solution of Eq 5A is of the form $N_1 = f(\lambda)$ where

$$\lambda = \frac{x}{\sqrt{t}},$$

it follows that the position of any point defined in terms of λ , or hence in terms of any combination of λ , N_1 , N_2 , D_1 , and D_2 , is given by the relation $x = I t^{1/2}$ where I is a function of λ , hence, constant for the type of point under consideration. Eq 8 for the velocity of a marker may

also be written $v t^{1/2} = (D_1 - D_2) \frac{dN_1}{d\lambda}$. As

$v t^{1/2}$ is a function of the position of a marker, initially at the join, and, as seen from the right side of this equation, is a function of λ , as N_1 , D_1 , D_2 are functions of λ , it follows that the position of such a marker x_m satisfies the above condition and is therefore given by the expression.

$$x_m = I t^{1/2} \quad \text{Eq 9}$$

or

$$v = \frac{dx_m}{dt} = \frac{1}{2} I t^{-1/2} = \frac{x_m}{2t} \quad \text{Eq 9a}$$

(which applies only to a marker initially at the join).

The validity of Eq 9 may be checked by the experimental data of Smigelskas and Kirkendall. The shift of interface (in cm) x_m , as given by them in their Table 1 is plotted against the square root of time (in days) in Fig 1. The deviations from linearity appear to be within the experimental error. From

this plot it is found that $\frac{dx_m}{dt^{1/2}} = 0.0016$ cm

day^{-1/2} or $v t^{1/2} = 0.0008$ cm days^{-1/2} = 2.72×10^{-6} cm sec^{-1/2}. Further experimental support of the foregoing reasoning that the position of the marker is a function of λ is found in the fact that the composition in the vicinity of the marker used by Smigelskas and Kirkendall is independent of time, being 22.5 pct zinc for both the 6 day and the 56 day samples.

For the 56 day sample (see penetration curve in Fig 3 of paper by Smigelskas and Kirkendall) the slope $\frac{dN_1}{dx}$ at the molyb-

TABLE I—Comparison of Observed and Calculated Diffusivity for the Silver-gold System

	800°C	900°C	1000°C
$D_1^* = 0.12\epsilon \frac{-44100}{RT}$	1.3×10^{-10}	7×10^{-10}	3.2×10^{-9}
$D_1^* = 0.39\epsilon \frac{-44700}{RT}$	3.1	18.	8.2
$D = 0.14\epsilon \frac{-41700}{RT}$ (observed)	4.5	24.	9.7
D calculated from Eq 18	3.8	21.	9.3

denum marker is 0.43 cm^{-1} , ignoring the difference between atom and weight per cent. As $l^{1/2} = 2.2 \times 10^3 \text{ sec}^{1/2}$, it follows from the above value of v $l^{1/2}$ that $v = \frac{2.72 \times 10^{-6}}{2.2 \times 10^3} = 1.24 \times 10^{-9} \text{ cm per sec}$. Inserting these values in Eq 8 it is found that $D_{Zn} - D_{Cu} = \frac{1.24 \times 10^{-9}}{0.43} = 2.9 \times 10^{-9} \text{ cm}^2 \text{ per sec}$ in the 22.5 pct zinc-copper alloy at 785°C . From the data of

Rhines and Mehl,⁸ $D = 4.5 \times 10^{-9}$ at 785°C and 22.5 pct zinc. Eq 7 and 8 thus become

$$\begin{aligned} D_{Zn} - D_{Cu} &= 2.9 \times 10^{-9} \text{ cm}^2 \text{ per sec} \\ 0.775 D_{Zn} + 0.225 D_{Cu} &= 4.5 \times 10^{-9} \text{ cm}^2 \text{ per sec} \end{aligned}$$

The solution is $D_{Cu} = 2.2 \times 10^{-9} \text{ cm}^2 \text{ per sec}$ and $D_{Zn} = 5.1 \times 10^{-9} \text{ cm}^2 \text{ per sec}$. The ratio D_{Zn}/D_{Cu} is 2.3, in fortuitously good agreement with the value 2.3 calculated by

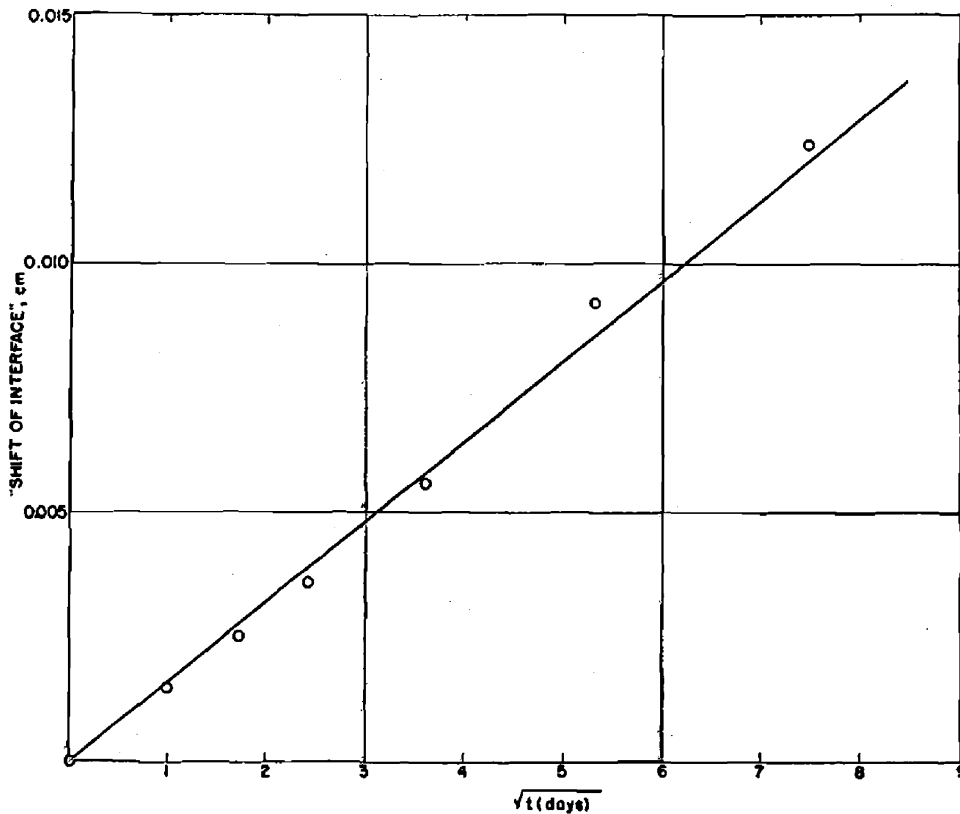


FIG 1—DATA OF SMIGELSKAS AND KIRKENDALL FOR DIFFUSION IN BRASS PLOTTED TO SHOW LINEAR VARIATION OF SHIFT IN POSITION OF INERT MARKERS WITH SQUARE ROOT OF TIME OF DIFFUSION IN ACCORDANCE WITH EQ 9.

the author from the data of Smigelskas and Kirkendall only.*

It is to be remembered that all the foregoing calculations are based on the assumption that the gram atomic volume is essentially constant. Although this condition is not satisfied too well by the solid solutions of zinc in copper, it seems reasonable that this should not give rise to serious error. The effect of any appreciable porosity in the high zinc side may be more serious though this effect is difficult to evaluate. Since Smigelskas and Kirkendall used only one set of markers, at the original join, D_{Zn} and D_{Cu} cannot be evaluated by this method at other compositions except at very low zinc content where it will be noted from Eq 7, $D = D_{Zn}$ which, from the data of Rhines and Mehl, is 0.3×10^{-9} . Thus D_{Zn} undergoes a 17 fold increase between 0 and 22.5 pct zinc.

The Relation between Diffusivity, Mobility and Activity in Binary Systems.

The force acting on a particle in a potential field is the negative gradient of its potential energy. In the case of atoms in a concentration gradient the potential per gram atom is assumed to be the Gibbs chemical potential, usually called the partial molal free energy. The diffusion velocity of an atom may be equated formally to the product of this force $-\frac{1}{N} \frac{d\bar{F}_2}{dx}$ and the velocity per unit force or mobility, B_2 ; hence the rate of linear diffusion of component 2 in gram atoms per unit time across a unit plane normal to the direction of diffusion is equal to the diffusion velocity times the concentration, or $-\frac{1}{N} \frac{d\bar{F}_2}{dx} \cdot B_2 C_2$, where N is

Avogadro's number. From the definition of D_2 , this rate is also equal to the expression $-D_2 \frac{dC_2}{dx}$.

Equating these two expressions

$$D_2 \frac{dC_2}{dx} = \frac{1}{N} \frac{d\bar{F}_2}{dx} B_2 C_2 \quad \text{Eq 10}$$

or

$$D_2 = \frac{d\bar{F}_2}{dC_2} \frac{B_2 C_2}{N} \quad \text{Eq 10a}$$

Using again the approximation that the gram atomic volume is constant

$$D_2 = \frac{1}{N} \frac{d\bar{F}_2}{dN_2} B_2 N_2 \quad \text{Eq 10b}$$

From the definition of activity, namely, $d\bar{F}_2 = RT \, d \ln a_2$, it follows, in combination with 10b that

$$D_2 = kTB_2 \frac{d \ln a_2}{d \ln N_2} \quad \text{Eq 11}$$

and from the definition of the activity coefficient, $\gamma_2 = a_2/N_2$

$$D_2 = kTB_2 \left(1 + N_2 \frac{d \ln \gamma_2}{d N_2} \right) \quad \text{Eq 12}$$

The analogous expression to Eq 12 for component 1, obtained by replacing all subscripts 2 with 1, is obviously equally valid.

$$D_1 = kTB_1 \left(1 + N_1 \frac{d \ln \gamma_1}{d N_1} \right) \quad \text{Eq 12a}$$

There is no intention to imply that the mobilities B and B_2 remain constant with varying composition. If the system is ideal, the activity coefficient is constant and this expression reduces to the well known Einstein relation⁹ $D_i = kTB_i$; the derivation of which is given in many places, for example by Jost.¹⁰ An equation similar to 12 has been given by Onsager and Fuoss¹¹ for the diffusion of electrolytes in aqueous solution. The contribution of the term in parenthesis involving the activity coefficient in Eq 12 is usually by no means insignificant. The magnitude of this term for binary metallic systems, may be determined by investi-

* L. S. Darken Discussion of reference 1. It will be noted also that the above calculation based in part on the data of Rhines and Mehl eliminates the possibility pointed out by Smigelskas & Kirkendall (in their reply) that the ratio of mobility for diffusivity of zinc to copper may be much greater on account of porosity effects in their samples.

gating a system which behaves regularly, that is, one for which $\ln \gamma_2 = \alpha N_1^2$, a relation followed approximately by many metallic systems (for an ideal system $\alpha = 0$). For such a system $N_2 \frac{d \ln \gamma_2}{d N_2} = -2\alpha N_1 N_2$.

Cases are known in which the absolute value of α is greater than 5, α being negative. For such a case the above term takes the value 2.5 for the 50-50 alloy; the expression in parenthesis in Eq 12 is 3.5 instead of unity as assumed in the Einstein relation.

It will be noticed that the equations developed so far in this part apply to a multicomponent system as well as to a binary system except for the coupling of irreversible processes which leads to the thermoelectric phenomena, the Soret effect and others. A binary system which obeys an equation of state, that is, all intensive properties are a function of temperature, pressure and composition only, obeys also the thermodynamic relation (Gibbs-Duhem equation),

$$N_1 d\bar{F}_1 + N_2 d\bar{F}_2 = 0 \quad \text{Eq 13}$$

which may also be written in terms of the activity coefficients

$$N_1 d \ln \gamma_1 + N_2 d \ln \gamma_2 = 0 \quad \text{Eq 13a}$$

or, since $dN_1 = -dN_2$,

$$N_1 \frac{d \ln \gamma_1}{d N_1} = N_2 \frac{d \ln \gamma_2}{d N_2} \quad \text{Eq 13b}$$

Hence it is seen that the expression in parenthesis in Eq 12 is equal to the corresponding expression in Eq 12A. Dividing Eq 12 by Eq 12A, it is seen that the following relation holds for such a binary system:

$$\frac{D_2}{D_1} = \frac{B_2}{B_1} \quad \text{Eq 14}$$

Since the isotope tracer technique is becoming popular as a method of measuring diffusion rates, it is of interest to investigate the relation between diffusivity determined in this manner and that determined by the

usual method of chemical analysis. In the case of a single element, the major isotope or mixture may be regarded as component one and the tracer isotope as component two. From Eq 7 ($D = N_1 D_2 + N_2 D_1$) it is seen that the diffusivity D , in this case, is equal to D_2 , since N_2 is very small. Thus, as may have seemed obvious beforehand, the diffusivity determined by this technique is that of the isotope tracer. Assuming that the properties of the isotope tracer are essentially identical with those of the major isotope, or isotopes, except for the slight difference in mass, it follows that the drift velocity ("stationary velocity") under unit force is essentially the same for the two, or that $B_1 = B_2$. From Eq 14 it then follows that $D_1 = D_2$ or that the term "self-diffusivity" as commonly applied is justified.

A very interesting set of experiments has been performed by W. A. Johnson¹² in which the diffusivity D , called by Johnson the "chemical diffusivity," was determined in the usual manner for the gold-silver system near the composition $N_1 = N_2 = 0.5$; in addition the diffusivity of radio-active gold and silver isotopes in this alloy was measured. In this case also there would seem to be very strong reason for the presupposition that the mobility (drift velocity under unit force) B_2^* , of the radioactive gold isotope is essentially the same as that of the rest of the gold, B_2 and similarly for the silver, that $B_1^* = B_1$. If the gold-silver solid solutions behaved ideally then it would be expected from the Einstein relation that $D_2^* = D_2$ and $D_1^* = D_1$; hence from Eq 7 that $D = \frac{D_1^* + D_2^*}{2}$ for the 50-50 alloy.

However it is found experimentally that such is not the case and that instead of being the mean of D_1^* and D_2^* , D is appreciably larger than either. Regarding this as an indication that departures from ideal

* The asterisk is used throughout this section to indicate a property of a radioactive trace isotope.

solution behavior may be significant, the problem will now be treated by means of Eq 12 and 7, which are believed to be exact except for changes in the gram atomic volume, and the above postulate as to the equality of mobilities of isotopes of the same element. Combining these two equations it is found for the "chemical case" that

$$D = kT \left(1 + N_2 \frac{d \ln \gamma_2}{dN_2} \right) / (N_1 B_2 + N_2 B_1) \quad \text{Eq 15}$$

For the case of the radioactive gold tracer Eq 12 becomes

$$D_2^* = kTB_2^* \left(1 + N_2^* \frac{d \ln \gamma_2^*}{dN_2^*} \right).$$

The activity coefficient is a function of the gross composition only and is not a function of the amount of trace elements or isotopes (see Henry's law), hence γ_2^* does not vary over the very small range allowed N_2^* and $N_2^* \frac{d \ln \gamma_2^*}{dN_2^*}$ is zero. In addition according to the above assumption $B_2^* = B_2$ and hence this relation becomes

$$D_2^* = kTB_2 \quad \text{Eq 16}$$

A similar relation obviously holds for the radioactive silver isotope

$$D_1^* = kTB_1 \quad \text{Eq 17}$$

Eliminating B_1 and B_2 from Eq 15 by means of Eq 16 and 17 it is found that

$$D = (N_1 D_2^* + N_2 D_1^*) / \left(1 + N_2 \frac{d \ln \gamma_2}{dN_2} \right) \quad \text{Eq 18}$$

In order to check this equation against Johnson's experimental data it is necessary to evaluate the term involving the activity coefficient. This may be done from the data of Wagner and Engelhardt¹³ who measured the activity of silver in silver-gold alloys over the concentration range $N_{Ag} = 0.0825$ to 1.00 by the electromotive force method; the temperature range was 407 to 745°C.

Plotting their data as $RT \ln \gamma_{Ag}$ vs. $(1 - N_{Ag})^2$ at the four temperatures investigated, as well as those of Wachter¹⁴ at 200 and 400°C, yields the curve shown in Fig 2. The line as drawn is the best straight line through the points corresponding to the data at 745°C, the highest temperature investigated; as the change with temperature seems to be less than the experimental error, this line will be regarded as representative of all temperatures considered. It is clear from this figure that the relation is essentially linear except for the last point of Wagner and Engelhardt at $N_{Ag} = 0.0825$, which is caused probably by an experimental error, as the point corresponding to this composition is very erratic at all temperatures investigated. However this may be, it is not important for the present consideration as we are interested in the behavior only at $N_2 = N_1 = 0.50$, which corresponds to $(1 - N_2)^2 = 0.25$ in Fig 2, where there is little question of the linearity of the plot. The slope $\left[RT \frac{d \ln \gamma_{Ag}}{d(1 - N_{Ag})^2} \right]$ as read is 3200 cal. From this slope values of the quantity $\left(1 + N_{Ag} \frac{d \ln \gamma_{Ag}}{dN_{Ag}} \right)$ are readily calculable at various temperatures. Values of D at $N_2 = N_1 = 0.5$, calculated from the experimentally determined values of D_1^* and D_2^* with the aid of these data and Eq 18, are shown in Table I. D_1^* , D_2^* , and D , all taken from a smoothed plot of Johnson's experimental data, are also given in this table.

The discrepancy between observed and calculated values, which averages about 10 pct does not seem too great to be attributed to experimental error; if the slope, $RT \frac{d \ln \gamma_{Ag}}{d(1 - N_{Ag})^2}$ had been taken from the lower points in Fig 1 then the calculated value of D would be increased by about 10 pct and would thus be in nearly perfect agreement with the observed values. The precision of the diffusion measurements as judged from the departure of the individual

points from the best straight line (Fig 8 of Johnson's paper) is about 5 pct.

It is of interest at this point to compare the above treatment of diffusion in the

that the diffusion process can be interpreted in terms of the activity gradient but if such is the case one would not expect to have to inquire further as to the source of the ac-

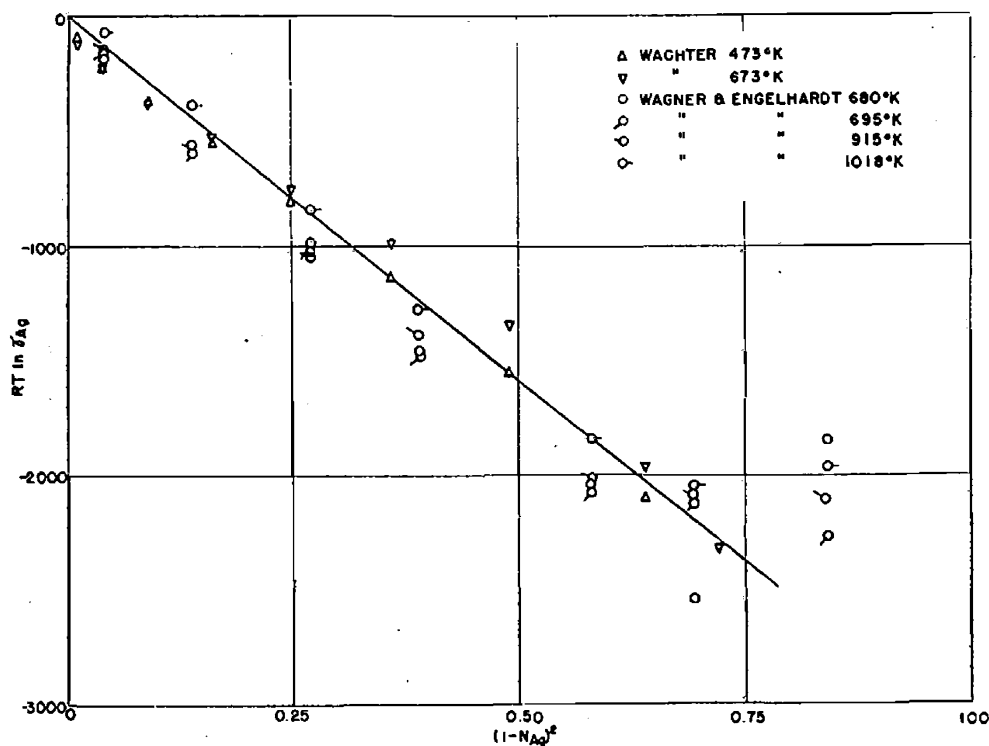


FIG 2—VARIATION OF ACTIVITY COEFFICIENT OF SILVER IN SILVER-GOLD ALLOYS, EXPRESSED AS $RT \ln \gamma_{Ag}$, AS A FUNCTION OF CONCENTRATION, $(1 - N_{Ag})^2$.

silver-gold system with that suggested by Birchenall and Mehl,² who favor a mechanism of diffusion involving a "direct interchange of lattice sites by two neighboring atoms." They further "assume that transport of gold in the alloy occurs chiefly by double exchange with silver and only to a negligible extent by exchange with itself." In other words, they assume that the mobility of the gold in a given alloy depends on the nature of the force acting upon it; that a different mobility will be observed if different forces identical in magnitude but different in nature act upon it. In one case the force derives from a composition (activity) gradient common to two gold isotopes and in the other from a composition gradient common to gold and silver. This appears to indicate a major inconsistency in their treatment. They postulate

activity gradient. If the treatment given by Birchenall and Mehl is correct then the concept of mobility is fruitless in diffusion, because the mobility, being the steady state velocity under unit force, becomes meaningless if the steady state velocity depends not only on the magnitude of the force but also on its nature. Although this is a possibility it is quite foreign to traditional physical thinking, a force of given magnitude having always been regarded as producing its effect, no matter what the origin or nature of the force. It is this traditional concept which has been utilized in this paper and which appears to give a quite satisfactory interpretation of Johnson's measurements. The fact that this concept is incompatible with the atomic interchange theory of diffusion seems to

this author to be further evidence that direct atomic interchange is very improbable.

SUMMARY

1. The recent experimental evidence of Smigelskas and Kirkendall, as to the motion of small inert markers during diffusion in brass suggests that the diffusivity as commonly defined is an inadequate representation of diffusion phenomena. The use of two diffusivities in binary systems—one for each component—has been proposed. In the case of diffusion accompanied by no change in the total volume this leads to a rather simple solution involving a reference frame rigidly fixed in the distant parts of the specimens and retaining the Boltzmann (or Matano) D , but requiring in addition a knowledge of the motion of inert markers imbedded in the alloy in which the diffusion occurs. The two simultaneous equations are

$$D = N_1 D_2 + N_2 D_1$$

$$\text{and } v = (D_2 - D_1) \frac{\partial N_2}{\partial x}$$

where D_1 and D_2 are the individual diffusivities of components one and two, N_1 and N_2 are atom fractions, x distance and v the velocity of an inert marker. Thus from D , as determined in the usual manner, and v , as determined by observation of inert markers, D_1 and D_2 may be evaluated from the above equations. This is done for the copper brass system.

2. Regarding the driving force in diffusion as the negative gradient of the chemical potential (partial molal free energy) the following relation between diffusivity D_i , mobility, B_i and activity coefficient, γ_i , is developed:

$$D_i = kTB_i \left(1 + N_i \frac{d \ln \gamma_i}{dN_i} \right)$$

This equation is an extension of the Einstein relation ($D_i = kTB_i$), which, however, is applicable only to systems obeying the ideal solution laws.

By combination of these relations it is

found that the diffusivity D , of a binary alloy is given by the expression

$$D = (N_1 D_2^* + N_2 D_1^*) \left(1 + N_2 \frac{d \ln \gamma_2}{dN_2} \right)$$

where the asterisk denotes a diffusivity determined by tracer technique in an alloy of the same composition. This relation is checked against available data and found satisfactory.

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DISCUSSION

(*J. W. Halley and W. T. Lankford, Jr. presiding*)

A. D. LECLAIRE*—The derivation of the expression for the velocity of a marker at the join surely involves the assumption in the first place that the concentration there is constant. Therefore, the observed fact that this is so, in Smigelskas and Kirkendall's experiments, is not a support of the truth of Darken's Eq 9 and 9a, but rather an indication that in this case (Zn in α -Brass) Eq 9 and 9a are applicable.

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The velocity of any marker is given by

$$v = (D_1 - D_2) \frac{\partial N_1}{\partial x}$$

$$\text{or } vt^{1/2} = (D_1 - D_2) \frac{\partial N_1}{\partial x} \quad \text{since } N_1 = f(\lambda).$$

The values of D_1 and D_2 at the position of the marker are functions only of the concentration at that position, therefore

$$vt^{1/2} = F(\lambda) = \left(\frac{\partial x}{\partial t} \right)_{\text{Marker}} t^{1/2}$$

$$\text{and } x = \int \frac{F(\lambda)}{t^{1/2}} dt + \text{constant} \quad [19]$$

If now we assume that the composition at the marker remains constant, $F(\lambda)$ is constant and goes outside the integral sign, when we have

$$x = 2t^{1/2}F(\lambda) + \text{constant} \quad [20]$$

at

$$t = 0, \quad x = x_0(\text{say}) \quad \text{and}$$

$$\therefore x - x_0 = 2vk$$

$$\text{or Velocity} = v = \frac{x - x_0}{2t} = \frac{\text{Shift of Marker}}{2t} \quad [21]$$

as obtained by Dr. Darken.

The only way of integrating Eq 19 to give Eq 21 seems to be to assume that $F(\lambda)$, and therefore the concentration, is constant.

Let us examine the conditions under which we might expect the composition at a marker to remain constant. Taking coordinates fixed in the end of the diffusing couple, Darken finds

$$\frac{\partial N_1}{\partial t} = \frac{\partial}{\partial x} \left(\{N_1 D_2 + N_2 D_1\} \frac{\partial N_1}{\partial x} \right)$$

Taking axes fixed with respect to a marker, moving with velocity v relative to the first set,

$$\frac{dN_1}{dt} = \frac{\partial N_1}{\partial t} + v \frac{\partial N_1}{\partial x}$$

where dN_1/dt is the total rate of change of concentration at the marker as it moves. We wish to know the conditions under which dN/dt is zero. Inserting the appropriate expressions in

[21] we find

$$\begin{aligned} \frac{dN_1}{dt} &= \frac{\partial}{\partial x} \left(\{N_1 D_2 + N_2 D_1\} \frac{\partial N_1}{\partial x} \right) \\ &\quad + (D_1 - D_2) \left(\frac{\partial N_1}{\partial x} \right)^2 \\ &= (N_1 D_2 + N_2 D_1) \frac{\partial^2 N_1}{\partial x^2} + \left(\frac{\partial N_1}{\partial x} \right)^2 \\ &\quad \left\{ N_2 \frac{\partial D_1}{\partial N_1} + N_1 \frac{\partial D_2}{\partial N_1} \right\} \quad [22] \end{aligned}$$

There is no information available at the moment to enable us to evaluate the last term accurately—it will be zero when D is independent of concentration. At other times, if we assume rates of change of D_1 , and D_2 with N_1 to be numerically the same, it will be approximately $(\partial N_1/\partial x)^2 \partial D_1/\partial N_1$ and therefore in general always finite. The first term will only be zero at a point of inflexion in the $N_1 \sim x$ curve, and such a point is usually in the neighborhood of the join.

We can then expect dN_1/dt to have a minimum value, at least, in the neighborhood of the join so that Darken's result Eq [1] is most likely to be valid for markers placed there. Since Smigelskas and Kirkendall's results support Eq 1, we must assume that dN_1/dt is around zero in their experiments, but it is clearly not justifiable to use [21] in the general case, even for markers at the join, without first testing that the concentration there is constant by plotting x against $t^{1/2}$ and seeing if a straight line corresponding to Eq [20] is obtained.

With regard to the second part of the paper, I feel that Dr. Darken has dismissed far too summarily the possibility of an atom for atom exchange process for the interdiffusion of Ag and Au and would suggest that the "major inconsistency" lies surely not in Birchenall and Mehl's treatment of Johnson's results but rather in Dr. Darken's conception of the meaning of "mobility."

Let us derive an expression for the Diffusion Coefficient for the case of an atomic exchange process, corresponding to Eq 12 of Dr. Darken for a single atom process. Consider first a binary solid solution of atoms A and B in which diffusion is occurring by place exchange. We are only interested in following the diffusion of A say, in exchanges of A with B since exchanges of A with A lead to no observable change.

* See eq. Lamb's "Hydrodynamics," p. 3. 6th Ed.

During an exchange of A with B , the force acting on A , f_{AB} is given, when μ_A and μ_B are the chemical potentials of A and B respectively, by

$$f_{AB} = -\frac{1}{N} \left\{ \frac{\partial \mu_A}{\partial x} - \frac{\partial \mu_B}{\partial x} \right\} \quad [23]$$

and is numerically equal to f_{BA} the force acting on B (as expected since there is no motion of the C. of G. of the AB pairs during the exchange). We now define a mobility term G_{AB} such that when unit force acts on an atom of A , G_{AB} is the average velocity with which this atom moves during the time taken for a complete A to B , B to A exchange process, which includes the time spent by the A atom as a neighbor to the B atom before the exchange occurs. The mobility of atoms B under similar conditions may be defined as G_{BA} , but by the very nature of the process and the equality of f_A and f_B G_{AB} and G_{BA} are equal.

The average velocity of an atom A during AB exchanges is then

$$C_A = -\frac{G_{AB}}{N} \left(\frac{\partial \mu_A}{\partial x} - \frac{\partial \mu_B}{\partial x} \right)$$

Δn_A , the number of atoms of A crossing unit area per unit time, along the x axis is equal to the number of atoms of A in volume C_A multiplied by the fraction of the neighbor of A which are, on the average, of Type B , (viz. N_B), since only AB interchanges are observable. (In accordance with this we note that $f_{AA} = f_{BB} = 0$.)

If n_A is the number of atoms of A per unit volume, and N_B the mol fraction of B

$$\Delta n_A = -N_B n_A \frac{G_{AB}}{N} \left(\frac{\partial \mu_A}{\partial x} - \frac{\partial \mu_B}{\partial x} \right)$$

This leads, if we assume $n_A + n_B = \text{constant}$, to

$$\frac{\partial N_A}{\partial t} = \frac{\partial}{\partial x} \left\{ G_{AB} k T \left(1 + N_A N_B \left\{ \frac{\partial \log \gamma_A}{\partial N_A} + \frac{\partial \log \gamma_B}{\partial N_B} \right\} \right)^{\partial N_A / \partial x} \right\} \quad [24]$$

where γ_A and γ_B are the activity coefficients of A and B . Therefore

$$D_{AB} = G_{AB} k T \left(1 + N_A N_B \left\{ \frac{\partial \log \gamma_A}{\partial N_A} + \frac{\partial \log \gamma_B}{\partial N_B} \right\} \right) \quad [25]$$

and by employing the Gibbs-Duhem relation for a binary solution

$$D_A = G_{AB} k T \left(1 + \frac{\partial \log \gamma_A}{\partial \log N_A} \right)$$

which is of exactly the same form as Eq 12 of Darken.

Now when there are more than two atoms present, e.g. atoms A , B and C , then A atoms can migrate by exchanging with A , B or C atoms. But only AB and AC exchanges lead to any observed change in the system and since the activation energies for these two processes will, in general, be different, the mobilities as defined above for the two processes will differ also. If the mobilities as defined above for the two processes will differ also. If we repeat the above derivation for a ternary system we find, in place of [25]

$$D_A^{II} = G_{AB} k T N_A N_B \left\{ \frac{\partial \log N_A \gamma_A}{\partial N_A} - \frac{\partial \log N_B \gamma_B}{\partial N_A} \right\} + G_{AC} k T N_A N_C \left\{ \frac{\partial \log N_A \gamma_A}{\partial N_A} - \frac{\partial \log N_C \gamma_C}{\partial N_A} \right\} \quad [26]$$

These relations [25] and [26] are to be discussed more fully in a forthcoming publication.

Let us now apply these results to Johnson's experiments. For the "chemically" observed diffusion of Au and Ag, we have the equation

$$(D_{Au})_{\text{chem}} = G_{AuAg} k T \left(1 + \frac{\partial \log \gamma_{Ag}}{\partial \log N_{Ag}} \right) \quad [27]$$

For the Self-diffusion experiment with Au, we have in effect a ternary system Ag, Au and Au* in which the diffusion of Au* is being observed.

$$D_{Au^*} = G_{Au^*Au} k T N_{Au^*} N_{Au} \left(\frac{\partial \log N_{Au^*} \gamma_{Au^*}}{\partial N_{Au^*}} - \frac{\partial \log N_{Au} \gamma_{Au}}{\partial N_{Au^*}} \right) + G_{Au^*Ag} k T N_{Au^*} N_{Ag} \left(\frac{\partial \log N_{Au^*} \gamma_{Au^*}}{\partial N_{Au^*}} - \frac{\partial \log N_{Ag} \gamma_{Ag}}{\partial N_{Au^*}} \right) \quad [28]$$

Now in Johnson's experiments the sample was chemically quite homogeneous and the only concentration gradient was that of radioactive gold. Therefore $dAu^* = -dAu$ and $dN_{Ag}/dN_{Au^*} = 0$ and since we can assume that the activity coefficient of gold is inde-

pendent of the proportion of radio-active gold it contains, the activity coefficients are everywhere constant and Eq (28) becomes

$$D_{Au^*} = G_{AuAu^*}kT(N_{Au} + N_{Au^*}) + G_{Au^*Ag}kTN_{Ag}$$

And since $(N_{Au} + N_{Au^*}) = N_{Ag} = \frac{1}{2}$, we have

$$D_{Au^*} = \frac{1}{2}kT(G_{Au^*Au} + G_{Au^*Ag}) \quad [29]$$

Now Birchenall and Mehl assume in effect that $G_{AuAu^*} = 0$, and since we can also assume that $G_{Au^*Ag} = G_{AuAg}$, we have from [27] and [29]

$$D_{Au^*} = kT\frac{1}{2}G_{AuAg} = \frac{1}{2}(D_{Au})_{Chem} \left(1 + \frac{\partial \log \gamma_{Ag}}{\partial \log N_{Ag}}\right)^{-1}$$

$$\text{i.e. } (D_{Au})_{Chem} = 2 \left(1 + \frac{\partial \log \gamma_{Ag}}{\partial \log N_{Ag}}\right) D_{Au^*}$$

We can calculate $\left(1 + \frac{\partial \log \gamma_{Ag}}{\partial \log N_{Ag}}\right)$ from the data given by Darken and so compare the two sides of the equation.

Temp.	800°C	900°C	1000°C
$D_{Au^*} - (\text{obs}) \dots \dots$	$1.3 \cdot 10^{-10}$	7.10^{-10}	$3.2 \cdot 10^{-9}$
$\left(1 + \frac{\partial \log \gamma_{Ag}}{\partial \log N_{Ag}}\right)$ (from Darken)	1.73	1.68	1.635
$(D_{Au})_{Chem}$ Calculated	$4.5 \cdot 10^{-10}$	$23.5 \cdot 10^{-10}$	$10.45 \cdot 10^{-9}$
$(D_{Au})_{Chem}$ Observed	$4.5 \cdot 10^{-10}$	$24.0 \cdot 10^{-10}$	$9.7 \cdot 10^{-9}$
Darken's Value-Calc.	$3.8 \cdot 10^{-10}$	$21 \cdot 10^{-10}$	$9.3 \cdot 10^{-9}$

The agreement is at least as good, if not better, than that obtained by Darken on the assumption of a single atom process and there are certainly no grounds for rejecting Birchenall and Mehl's assumption of a place exchange process with $G_{AuAu^*} = 0$. There is hardly sufficient evidence to decide definitely between a single atom or two atom (exchange), diffusion process in this case. The near correspondence for the two mechanisms arises because, in this case, when N_{Ag} and N_{Au} are each equal to $\frac{1}{2}$, it so happens that

$$2D_{Au^*} = N_{Ag}D_{Au^*} + N_{Au}D_{Ag^*}$$

It would be most interesting to repeat Johnson's experiments and the above calculations

for some other alloy composition, when it might be possible to distinguish between the two mechanisms.

C. E. BIRCHENALL,* L. C. CORRÊA DA SILVA,* and R. F. MEHL*—In our discussion of this paper we will attempt to avoid overlap with remarks to follow the paper of Fisher, Hollomon and Turnbull scheduled for this afternoon. The activity correction for the diffusion process will be considered in connection with this latter paper which represents a more advanced stage in the theory because it grapples with the details of the mechanism of solid metallic diffusion and recognizes the role of the crystal lattice in diffusion as compared with the uncertain hydrodynamic flow concepts in the present paper. The lack of consideration of the mechanism of the diffusion process is a major weakness and makes pointed discussion difficult. Fisher, Hollomon and Turnbull demonstrate that the type of solution arrived at here is only one of many possibilities.

Another major difficulty of this paper is the fact that it is based on one experiment of questionable validity. If the conclusions derived from the Smigelskas and Kirkendall experiments should prove to be unfounded much of the present paper would not be pertinent to substitutional solid metallic diffusion, although it may apply to other diffusing systems. Our discussion will try to show that the other experiments referred to do not support the viewpoint of this paper, and that the Smigelskas and Kirkendall experiment, the only evidence supporting this point of view, contains serious inconsistencies. Let us consider first the other experiments mentioned here.

There seems to be no reason to doubt that ions of different metals diffuse at different rates in liquid mercury. This is probably true of solid mercury, but this is not evidence that the diffusion rate of mercury ions are unaffected by the foreign ions.

If a chip is thrown into a stream, be it of mercury, water, or brass, the chip will respond immediately to acceleration of the surrounding stream only if the chip surface is wetted by the stream. Otherwise slippage is likely to occur. Even liquid copper does not wet molybdenum.

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Nor is it easy to visualize the movement of a massive wire by a series of processes, the units of which probably involve not more than a few dozen atoms. In this regard, it would be enlightening to know the source for the statement that "ghost lines" and nonmetallic inclusions move in the same way as wire markers and similar "to the way chips of various materials move together in the stream of water." This implies that quantitative measurements of the movements of these "ghost lines" and inclusions exist for the interior of metal samples in which diffusion is occurring. We know of no such information.

It would seem useless at best, and perhaps quite misleading, to attempt to draw conclusions about metallic diffusion by analogy with ionic crystals. In the latter the components occupy different sets of lattice sites (similar in some respects to interstitial solid solutions such as austenite where the differences in the rates of diffusion of the interstitial and lattice components are known to be large). Except under conditions favoring superlattice formation, where diffusion rates are too low for measurement, substitutional metallic solid solutions make all sites available to all components of the solution.

On the same page as the experiments of Schwarz, a reference of R. P. Johnson¹⁵ contains the following concerning the migration of tungsten on electrically heated filaments: "Structure identical in form with the dc structure appears on the ac filaments where a temperature gradient exists, and is attributable directly to surface diffusion in the temperature gradient." So this non-isothermal experiment probably has nothing at all to say about the electrolytic transport of tungsten ions in bulk metal. To draw further conclusions about the behavior of alloying elements in such a system seems to us unwarranted. That solid solutions can be electrolyzed is well known, but when one component migrates toward the cathode, the other migrates toward the anode.

On the basis of this paper, the problem of choosing reference markers might appear to be a very difficult one. Actually investigators faced with the practical problem seem to have arrived at the same conclusion without benefit of drifting markers; if a lattice point is chosen

in the metal beyond the penetration zone, it will still be there after the diffusion anneal and will serve as a convenient reference. This is a standard practice.

On the basis of the well established theory of X ray diffraction, the relative position of equilibrium lattice points can be determined with a precision of the order of one hundredth of one percent. Furthermore, this long range order is one of the features which best distinguishes the solid metal from the liquid metal. In a diffusion measurement, the practically observable states of the system are the metallic crystal at room temperature prior to the diffusion anneal and the same crystal at room temperature subsequent to the anneal. A lattice point then has a rather precise meaning and is no less observable than are electrons.

We have found the remarks on the "nature" of forces affecting the diffusion process difficult to understand. They seem to derive from the notion that diffusion in substitutional solid solution may be treated as a unimolecular process, an assumption which seems doubtful in view of the work of Fisher, Hollomon and Turnbull. The mobility of a single ion is not necessarily independent of the directional properties of the field around it and the behavior of the neighboring ions.

Let us now turn to the Smigelskas and Kirkendall experiment. A review of the literature on diffusion in alpha brass will show that such studies are not without inherent risk. Diffusion coefficients for a given temperature vary far beyond any reasonable experimental error. Much of the difficulty is probably due to the volatility of zinc at diffusion temperatures. Further abnormalities may be due to the structure of plated copper, although it is by no means certain that this is the case. Vapor transport of zinc may possibly occur along grain boundaries of the plated copper or at the copper-brass interface without return of copper.

The shape of the penetration curves reported by Smigelskas and Kirkendall does not correspond to any of the many others reported in the literature, and is therefore suspect. If the 56 day data are plotted on probability paper, a nearly straight line is obtained for the high zinc part. At a position corresponding to the point where plating was discontinued to remove the

¹⁵ R. P. Johnson: *Phys. Rev.* **54**, 459 (1938).

glass rod supports for the molybdenum wires, the penetration data drop off very sharply. This suggests a possible discontinuity in the plated copper structure.

In some unpublished experiments on diffusion in alpha brass using cylindrical samples in this laboratory, George and Mehl observed that some samples showed evidence of creep during the diffusion anneal. Cross-sections which were initially circular became elliptical. This suggests an alternative mechanism for the transport of molybdenum wires with respect to each other. But it will not explain the shift with respect to the penetration curve which may have its origin in the effects mentioned above.

On a penetration curve one can locate the initial interface and the Matano interface corresponding to conservation of atoms in the diffusing system. Expressing the deviation between these interfaces in the percentage of the area under one half of the curve on one side of the Matano interface (a measure of the total transport) enclosed between this interface and the initial interface the results obtained for the data of Rhines and Mehl,¹⁶ George and Mehl,¹⁷ and Smigelskas and Kirkendall are those given in Table 2.

One may readily see from the deviations in the table that the Matano (equitransport) interface scatters about the initial interface. The scatter is probably due to errors in distance measurements and chemical analysis. Their magnitude amply illustrates the danger in arriving at general conclusions on the basis of a single experiment. Taking all the data into consideration, there seems to be no reason for accepting the results of the Smigelskas and Kirkendall experiment.

It is obvious that the solution to this problem is to be found in the laboratory and not at the desk. Critical experiments should avoid as much as possible the sources of uncertainty involved in working with alpha brass and copper plate. Such experiments on other alpha solid solutions of copper as well as repeat experiments on alpha brass are under way in this laboratory. Because of the extreme precision required, the work is necessarily slow.

Since the unit diffusion process occurs between two planes in a crystal lattice and is a

¹⁶ Rhines and Mehl: *Trans. AIME* (1938) 128, 185.

¹⁷ George and Mehl: not published.

property of the metallic crystal plotting the penetration curve in terms of the number of atoms per unit cell as ordinate against the number of lattice planes from some chosen reference plane as abscissa should give a fundamental representation of the process. The abscissa is not linear with distance, but it is independent of

TABLE 2—Comparison of Data

Sample	Maximum Zn Pct	Pct Deviation
Rhines and Mehl Samples		
28	13	12
29	13	98
31	13	-10
32	13	-14
33	13	27
34	13	-11
35	13	7
36	30	0
37	30	0
38	30	5
39	30	4
40	30	25
41	30	6
George and Mehl Samples		
P-1	28	-9
P-2	28	-12
Smigelskas and Kirkendall Samples		
6 day	30	55
56 day	30	25

temperature and composition and partially eliminates the volume changes accompanying diffusion. We propose this as the most satisfactory method for plotting diffusion data. An illustration for carbon diffusion in austenite is given here. (Fig 3.)

R. SMOLUCHOWSKI*—Although the author scrupulously avoided any explicit assumptions as to the mechanism of diffusion, there are some general implications which need clarification. The first is the notion of "force." It is so often assumed that in the process of diffusion there is an actual force "arising from concentration gradients" constantly acting on the individual atoms. On atomic scale this means that an atom eventually moves in the direction of that local "force" because of nonuniform distribution of the two kinds of atoms among its neighbors. It is important to realize that this is not necessarily true in the mechanical sense of the word "force" and that such an implication

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should be avoided: The fundamental question is not whether the field of force surrounding an atom in its equilibrium position *before* a jump is asymmetrical or not, but whether *after* the

plane parallel to the original interface is observed. Further discussions of this point will be given in connection with Dr. Hollomon's paper. (See p. 211.)

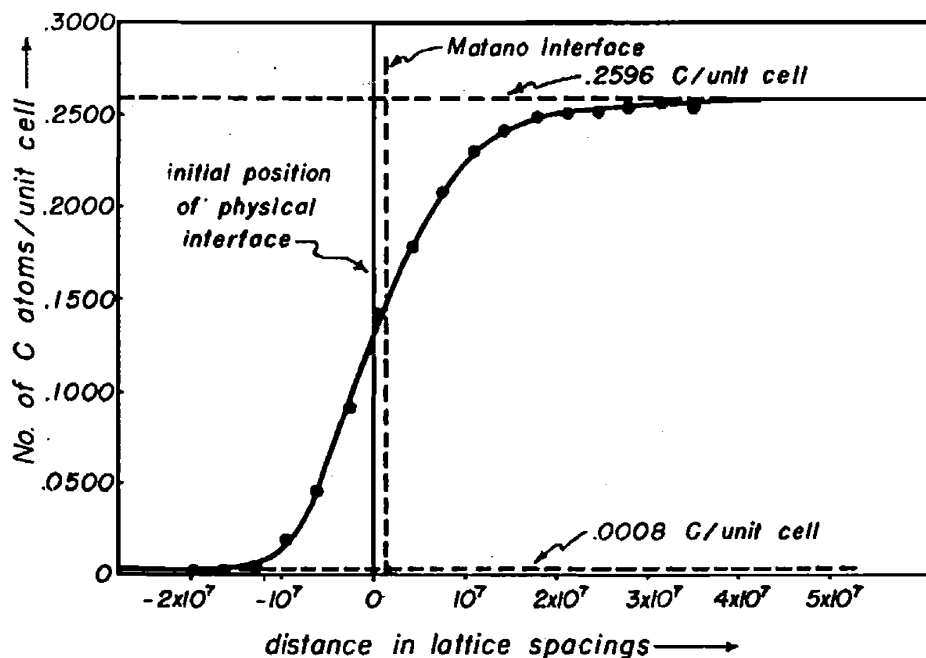


FIG 3—CARBON DIFFUSION IN AUSTENITE.

jump the atom finds itself in a state of higher or lower energy than it had before. To be sure, this point is not of significant importance in the author's interesting consideration.

Secondly, I would like to draw attention to a certain aspect of experiments performed with brass-copper couples which probably should be elucidated before any far-going theoretical conclusions are made. It is the difference of the atomic volumes of the two kinds of atoms which produces nonequal number of atoms per unit area of the interface. One could hardly expect an equal transfer of atoms in both directions under such conditions. This in turn may produce internal strains and even a network of oriented cracks, which would have a profound influence on the rate of diffusion. Naturally imperfections inherent in plated metal should be avoided as they may affect appreciably the kinetics of the observed phenomena and are probably responsible for the large scattering of experimental results.

The author's objections against the insistence on interchange of atoms is justified. It is, indeed, very seldom that an equal transfer of atoms in both directions through each atomic

J. H. HOLLOMON*—I believe that Darken's analysis of the two component diffusion case is excellent. Perhaps it might be wise to clear up briefly some of the points that the earlier discussers have made. It is unnecessary to talk about mechanism in analyzing the importance of Darken's paper. What he has said, I believe—and I would like his comments on this point—is that if the two components diffuse at different velocities, his treatment handles the problem. In other words, Dr. Darken does not really have to say anything about mechanism at all.

He says that if copper diffuses across a boundary more rapidly than zinc diffuses, then the interface must move. If the interface does move, how it will move is described in his paper. In other words, if markers move, there must be two diffusivities. If there are two diffusivities, then the two diffusivities must obey the equations that Dr. Darken has developed. Furthermore, if there are two diffusivities, then the markers must move.

Now, whether or not the markers move, or

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whether or not there are two diffusivities, is a matter that can be checked only by experiment. No amount of analysis can help us decide whether or not there are in actuality two diffusivities, or whether or not the markers move. However, if they do move, and if there are two diffusivities, then Dr. Darken's paper tells us how to treat the problem. Detailed discussions of the "truth" of the Kirkendall-Smigelskas experiments do not mitigate against the validity of Darken's analysis based on his assumptions.

L. S. DARKEN (author's reply)—With reference to most of the comments, Dr. Hollomon has furnished me with a reply better than I could make myself. One point I should like to add is this: Dr. Birchenall states that the weakness of my paper lies in the lack of consideration of a mechanism. In my opinion, its strength lies in this very lack of consideration of mechanism.

The difference between the treatment given and that suggested by Dr. LeCaire seems to arise principally from the manner of extension of Eq 25 to ternary systems yielding Eq 26. Mobility is defined as the average drift velocity (at steady state) of the particle under consideration per unit force in the medium under consideration. Granting that in a ternary system, a given atom or ion can move by more than one mechanism, it is difficult to see how it can have more than one average velocity; Eq 26 of Dr. LeCaire's discussion seems to call for two average velocities or mobilities of the same species in the same lattice at the same time. It is to be hoped that the forthcoming publication which he promises will clarify this matter.

The first part of the present paper represented an attempt to devise a useful diffusion equation from a minimum number of assumptions of such nature that the equation would rest on as firm a foundation as possible and be general in scope. Hence no assumption whatever is made as to the mechanism of the diffusion process. In order to simplify the calculation, the assumption is made that the total volume does not change during diffusion; if this is not adequately satisfied in any particular case the solution may be extended to cover such contingency. It is assumed that the

calculus may be used; it is assumed that the law of conservation of matter holds. Aside from these the only fundamental physical assumption involved is that D_1 and D_2 as defined in terms of the chosen frame of reference are, at constant temperature and pressure, functions of composition only. The analogy made in the introduction to chips in water was intended to be merely explanatory; the derivation does not hinge thereon. The derivation of the velocity of a marker initially at the join involves no assumptions further than those stated above; the proof is given in the paper. Eq 9, of course, applies only to the position of markers initially at the join.

The second part of the paper utilizes the concept of force as the negative gradient of the free energy. In this connection, Onsager and Fuoss, conclude as result of a detailed physical and mathematical consideration, "We have shown above that potential gradients will cause the same migration of ions as equal forces." The gradient referred to, is that of the free energy as used in the present paper; inspection of their argument shows that the conclusion applies equally well to uncharged as to charged particles (ions). In addition to this it is assumed that the Gibbs-Duhem equation applies—that is, that the free energy is an extensive property; no surface or interface energies have been considered and hence the results could not properly be applied to a case involving grain boundary diffusion. Henry's law is assumed valid at low concentration. The assumptions of the first part of the paper are carried into the second part. No assumptions other than those just described are involved in Eq 18 which applies strictly only to an alloy containing a vanishingly small amount of tracer isotopes.

The author feels that the equations developed are general in nature, independent of the mechanism of any particular diffusion process and that they are in accord with the available experimental data which include: 1. The well established observations that the self-diffusivity of a metallic element differs from the diffusivity of another element at low concentration therein. 2. The experiments of Smigelskas and Kirkendall on the motion of inert markers. 3. The experiments of W. A. Johnson determining D , D_1^* and D_2^* a gold-silver alloy.