JOURNAL OF MATERIALS SCIENCE **20** (1985) 4317–4328

Reference planes for binary diffusion with variable molar volume

A. G. GUY
Department of Physics and Space Science, Florida Institute of Technology, Melbourne, Florida 32901, USA

Present-day treatments of diffusion in metallic solid solutions require an accurate, convenient analysis that takes account of the actual variations of atomic size with concentration. Recent research by the author has produced such an analysis, which employs ordinary Cartesian coordinates. The first and second Fick equations are essentially the same as the usual forms (for constant, equal atomic size), differing only in the addition of the factor $\bar{V}$, the total molar volume of the solid solution. The prevalent erroneous concept of an "invariant" for diffusion demonstrates the need for a clearer understanding of the role of reference planes in treatments of diffusion. Reference systems of two types are dicussed: conventional reference systems (Fick and molecular), and the lattice (Kirkendall) reference system. The diffusion velocity, v, of a given component is used as the basis for defining the diffusion flux. Absolute values of v can be determined from data on the Kirkendall shift, but only relative values ($v - \omega$) can be employed if only a conventional reference system is used in the analysis.

1. Introduction

In the past, most treatments of diffusion have been for the simple case of equal and constant partial molar volumes, $\bar{V}_1 = \bar{V}_2$, of the interdiffusing metals. A recent advance in the theory of vacancy diffusion [1] has shown that the magnitude of the independent vacancy flux produced during interdiffusion depends on the difference between $\bar{V}_1$ and $\bar{V}_2$. In particular, in the case of tin diffusing in a copper–tin solid solution, where $\bar{V}_{\mathrm{Sn}} = 1.85\,\bar{V}_{\mathrm{Cu}}$, the independent vacancy fluxes are so large that the copper atoms are forced to flow *up* their concentration gradient, resulting in a negative value for the intrinsic diffusion, D_{Cu} [1]. Even for more usual differences in atomic volume, the effect on vacancies is appreciable; therefore, a convenient treatment of diffusion for unequal, concentration-dependent partial molar volumes is needed for contemporary analyses of diffusion data.

In later sections of this paper it will be shown that correct treatments of interdiffusion can be made using the following simple forms of the first Fick law (Equation 28 of Section 2):

$$J_1 = \frac{-\tilde{D}}{\bar{V}}\frac{\mathrm{d}X_1}{\mathrm{d}x}$$

and of the second Fick law (Equation 69 of Section 5):

$$\frac{1}{\bar{V}}\frac{\partial X_1}{\partial t} = \frac{\partial}{\partial x}\left(\frac{\tilde{D}}{\bar{V}}\frac{\partial X_1}{\partial x}\right)$$

(Guy and Oikawa [1] used the symbol J_1 to refer to a flux relative to the crystal lattice; the present symbol for this type of flux will be ${}_{\mathrm{L}}J_1$. Similarly, they used ${}_{\mathrm{m}}J_1$ to refer to a flux relative to the molecular reference system; for convenience in the present paper this type of flux will be denoted by the symbol J_1.) Thus J_1 is the flux (measured in $\mathrm{mol\,m^{-2}\,sec^{-1}}$) of Metal 1 relative to the molecular reference system, $\tilde{D}$ is the usual interdiffusion coefficient, $\bar{V}$ is the total molar volume ($\mathrm{m^3\,mol^{-1}}$) at the point being considered,

0022–2461/85 \$03.00 + .12

X_1 is the concentration in mole fraction, x is the usual Cartesian coordinate, and t is time. For the special case $\bar{V}_1 = \bar{V}_2 =$ constant, the equations reduce to the usual forms of the Fick laws.

These equations are much simpler than the expressions proposed by previous investigators [2–10] and are free of other shortcomings (discussed below) of several of the earlier solutions. The treatments in the existing literature are extremely diverse because the nature of a given treatment depends on five independent choices made by the investigator. The features in question are listed below.

1.1. Coordinate system

This can employ either the usual Cartesian coordinate x, or a special coordinate ξ that varies with changes in total molar volume $\bar{V}$. In general, Cartesian coordinates are more convenient.

1.2. Reference point in specimen

This can be either an end of the specimen (far from the region of diffusion) or a Matano interface near the centre of the region of diffusion. The latter choice has both practical and theoretical advantages.

1.3. Conventional reference system

The two most common are the Fick (or volume-fixed) and the molecular (mole-fixed) reference systems. Essentially, equal volumes of Metals 1 and 2 cross the initial interface in the Fick systems, whereas equal numbers of moles cross the reference plane in the molecular system. A common error in the use of the Fick reference system occurs in connection with the construction of the Matano interface. The equations involving the fluxes ${}_{\mathrm{f}}J_1$ and ${}_{\mathrm{f}}J_2$ referred to the Fick reference system are

$$ {}_{\mathrm{f}}J_1 = -\tilde{D}\frac{\mathrm{d}C_1}{\mathrm{d}x} \qquad {}_{\mathrm{f}}J_2 = -\tilde{D}\frac{\mathrm{d}C_2}{\mathrm{d}x} \quad (1) $$

and involve concentrations C in mol m^{-3}. But on a plot of diffusion data as C against x, the Matano interface divides the plot in such a way that equal numbers of moles of Metal 1 and Metal 2 have crossed the interface; that is, $J_1 = -J_2$. A common (erroneous) conclusion is that ${}_{\mathrm{f}}J_1 = -{}_{\mathrm{f}}J_2$, but the error here is that J_1 and J_2 are referred to the molecular system, whereas the form of the first Fick law employed in Equation 1 is appropriate for the Fick reference system. The fluxes employed in Equation 1 are not equal and opposite but satisfy the following relation (see Equation 16):

$$ {}_{\mathrm{f}}J_1\,\bar{V}_1 = -{}_{\mathrm{f}}J_2\,\bar{V}_2 \quad (2) $$

1.4. Definition of $\tilde{D}$

If $\bar{V}_1 = \bar{V}_2 =$ constant, then the definition of the interdiffusion coefficient $\tilde{D}$ given by Equation 1 is correct both for the Fick and for the molecular reference systems. For variable partial molar volumes, there is general agreement that $\tilde{D}$ should be defined so that Equation 1 continues to be valid *for the Fick reference system*. A logical consequence, however, is that the corresponding form of the first Fick law for use with the molecular reference system is that given by Equation 28 (Section 2). The difference between Equations 28 and 1 is not due simply to a conversion between the concentration units X and C. If Equation 28 is written in terms of C the result is

$$ J_1 = \frac{-\tilde{D}\bar{V}}{\bar{V}_2}\frac{\mathrm{d}C_1}{\mathrm{d}x} \quad (3) $$

In fact, the difference is a logical result of the use of two different reference planes to determine the magnitude of the diffusive flux.

1.5. Inclusion of data on motion of markers (Kirkendall effect)

These data may or may not be available for a given diffusion curve. In the absence of such data, only $\tilde{D}$ (a single coefficient) can be determined as discussed in Section 2. With the aid of data on Kirkendall markers, two intrinsic diffusion coefficients, D_1 and D_2, can be determined. D_1 and D_2 satisfy the relation

$$ \tilde{D} = X_2 D_1 + X_1 D_2 \quad (4) $$

provided they are defined by the analogue of Equation 28 (Section 2).

In the metallurgical literature the subject of reference planes has usually been treated in a relatively elementary manner. Fortunately, the more advanced conceptual and mathematical problems connected with reference systems for diffusion are available in the literature of chemical engineering and of non-equilibrium thermodynamics. The methods described by Haase

[11] are employed here. Two types of reference systems are of interest. One type (lattice system) is physically present in a diffusion specimen: an array of Kirkendall markers is an example. This type will be considered in Section 3. The other type of reference system (conventional system) is not visible in the diffusion specimen, but instead is a construction created for experimental and/or theoretical convenience. A conventional reference system can always be employed in the analysis of diffusion data. The lattice system may be used (often in addition to a conventional system) provided the necessary observations have been made on appropriate markers in the diffusion specimen.

Although the analysis presented here applies for variable atomic volumes, schematic explanations will be given for constant, but unequal, atomic volumes of the two components; namely, $\bar{V}_1 = 2\bar{V}_2$. In this case no overall change in volume accompanies the process of diffusion between pure Metal 1 and Metal 2, assumed for simplicity to form a complete series of solid solutions. For convenience in explaining in Section 2 why two different conventional reference systems do not coincide, use will be made of the intrinsic diffusion coefficients, ${}_{\mathrm{f}}D_1$ and ${}_{\mathrm{f}}D_2$, of the two components. Each will be assumed to be constant and their ratio will be taken as ${}_{\mathrm{f}}D_2/{}_{\mathrm{f}}D_1 = 5$. It should be recognized, however, that such detailed information cannot be obtained from the data discussed in Section 2 but only with the aid of additional data available from use of the lattice reference system (Section 3).

2. Conventional reference systems

Fig. 1a shows the maximum amount of experimental data that could be obtained from an experiment involving the interdiffusion of a specimen which, prior to the diffusion treatment, consisted of a bar of length L of pure Metal 1 welded to a similar bar of pure Metal 2. Although the midpoint L of the diffused specimen can be located by a measurement from an end of the bar, a reference plane at this point does not possess the generality desirable for the analysis of the diffusion data. Concentrations C_1 and C_2 are related by the equation

$$C_1\bar{V}_1 + C_2\bar{V}_2 = 1 \qquad (5)$$

and therefore only one concentration gradient is independent. The relation between the two

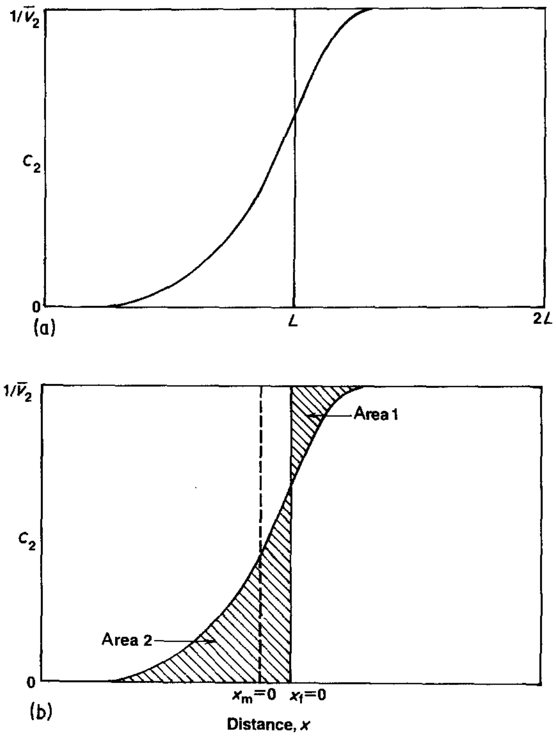

Figure 1 (a) Typical diffusion curve for the interdiffusion of Metals 1 and 2 described in the text. The concentration unit for C_2 is moles per unit volume. (b) The origin $x_{\mathrm{f}} = 0$ of the Fick reference system coincides with the midpoint L shown in (a). Areas 1 and 2 are in the ratio $\bar{V}_2/\bar{V}_1$, but the interface at $x_{\mathrm{m}} = 0$ divides the diffusion curve into two equal areas.

gradients, even for the case of variable partial molar volumes, is

$$\frac{\mathrm{d}C_1}{\mathrm{d}x} = -\frac{\bar{V}_2}{\bar{V}_1}\frac{\mathrm{d}C_2}{\mathrm{d}x} \qquad (6)$$

Because there is only one independent concentration gradient, there can be only one independent diffusion coefficient in an analysis involving a conventional reference system. The following analysis is for a typical volume element in a binary system that has undergone diffusion for some arbitrary period of time.

Rather than using the first Fick law (see Equation 17 below) to define a diffusion flux, we employ the relations

$$J_2 = C_2 v_2 \quad \text{and} \quad J_1 = C_1 v_1 \qquad (7)$$

where v_i is the diffusion velocity of an average atom of component i, C_i is concentration in moles of component i per unit volume, and J_i is therefore in units of moles per unit area per unit time. The velocities v_1 and v_2 must be measured relative to some reference velocity. For example, the velocity of the midpoint L could be used for this purpose, but this would be an arbitrary choice without general usefulness. A useful convention defines the reference system as moving with a velocity ω that is a weighted average of the diffusion velocities of the two components:

$$\omega = \beta_1 v_1 + \beta_2 v_2 \tag{8}$$

The weighting factors β_1 and β_2 are normalized so that

$$\beta_1 + \beta_2 = 1 \tag{9}$$

For example, we can weight v_1 and v_2 by the relative number of atoms of each component in the volume element; that is, by their mole fractions. Since $X_1 + X_2 = 1$ the condition of Equation 9 is immediately obtained without any need for normalization. The value of ω obtained in this manner

$$\omega_{\mathrm{m}} = X_1 v_1 + X_2 v_2 \tag{10}$$

represents the average velocity of the atoms of the two components and defines the *molecular reference system.* A second example, the *Fick reference system,* is based on the average velocity of the two components in terms of volume (rather than number of atoms). The appropriate weighting factors for use in Equation 8 are now the volume fractions, $C_1\bar{V}_1$ and $C\bar{V}_2$, of the two components

$$\beta_1 = C_1\bar{V}_1 \quad \text{and} \quad \beta_2 = C_2\bar{V}_2 \tag{11}$$

since the sum of the two volume fractions is unity as required in Equation 9. The value of ω obtained in this case is

$$\omega_{\mathrm{f}} = C_1\bar{V}_1 v_1 + C_2\bar{V}_2 v_2 \tag{12}$$

where ω_{f} is known as the mean volume velocity and defines the Fick reference system.

In general, the velocities relative to ω are $(v_1 - \omega)$ and $(v_2 - \omega)$. Therefore the diffusion fluxes are given by

$${}_{\omega}J_1 = C_1(v_1 - \omega) \quad \text{and} \quad {}_{\omega}J_2 = C_2(v_2 - \omega) \tag{13}$$

The numerical value of ${}_{\omega}J_i$ will depend, of course, on the convention used to define the reference velocity ω. From Equations 7, 8, 9 and 13 we obtain the general relation between the two diffusion fluxes

$$\frac{\beta_1}{C_1}\,{}_{\omega}J_1 = -\frac{\beta_2}{C_2}\,{}_{\omega}J_2 \tag{14}$$

Although the fluxes will be equal and opposite (the case considered in elementary treatments) if $\beta_1/C_1 = \beta_2/C_2$, they can be unequal for other choices of the reference system.

In the case of the Fick reference system defined by Equation 12, the diffusion fluxes are given by

$${}_{\mathrm{f}}J_1 = C_1(v_1 - \omega_{\mathrm{f}}) \quad \text{and} \quad {}_{\mathrm{f}}J_2 = C_2(v_2 - \omega_{\mathrm{f}}) \tag{15}$$

The following relation between these two fluxes is obtained by substituting in Equation 14 the values of β_1 and β_2 from Equation 11:

$${}_{\mathrm{f}}J_1\bar{V}_1 = -\,{}_{\mathrm{f}}J_2\bar{V}_2 \tag{16}$$

In this case equal *volumes* of atoms of Components 1 and 2 diffuse in opposite directions across reference planes. Consequently, the interface at which the bars of Metal 1 and of Metal 2 were initially joined (at L in Fig. 1a) is the origin of the Fick reference system (Fig. 1b).

A diffusion coefficient D that enters into the first Fick law, $J = -D(\mathrm{d}c/\mathrm{d}x)$, is not necessarily the usual interdiffusion coefficient $\tilde{D}$ that is widely employed in the literature on diffusion. Of the many possible fluxes defined by Equation 13, J must be the ${}_{\mathrm{f}}J$ defined by Equation 15. Of the many possible concentration units (such as mole fraction, X), $\mathrm{d}c/\mathrm{d}x$ must be in units of moles per unit volume, C (or this unit multiplied by a constant). Therefore, we write the first Fick law for Component 2 in the form

$${}_{\mathrm{f}}J_2 = -\tilde{D}\frac{\mathrm{d}C_2}{\mathrm{d}x} \tag{17}$$

$\tilde{D}$ has the same value for Component 1 as for Component 2, but in view of Equation 6,

$${}_{\mathrm{f}}J_1 = -\tilde{D}\frac{\mathrm{d}C_1}{\mathrm{d}x} = -\frac{\bar{V}_2}{\bar{V}_1}\,{}_{\mathrm{f}}J_2 \tag{18}$$

in agreement with Equation 16.

The Fick reference system and the concentration unit moles per unit volume, C_i, are closely connected. First, the C_i values are used in Equation 12 to define the reference velocity. Second, if the diffusion curve is plotted in terms of C_2, as in the example of Fig. 1a, then the origin of the Fick reference system divides the curve into two areas in the ratio $\bar{V}_2/\bar{V}_1$ as shown in Fig. 1b. Since the data are plotted in terms of C_2, it is convenient also to write Fick's law in

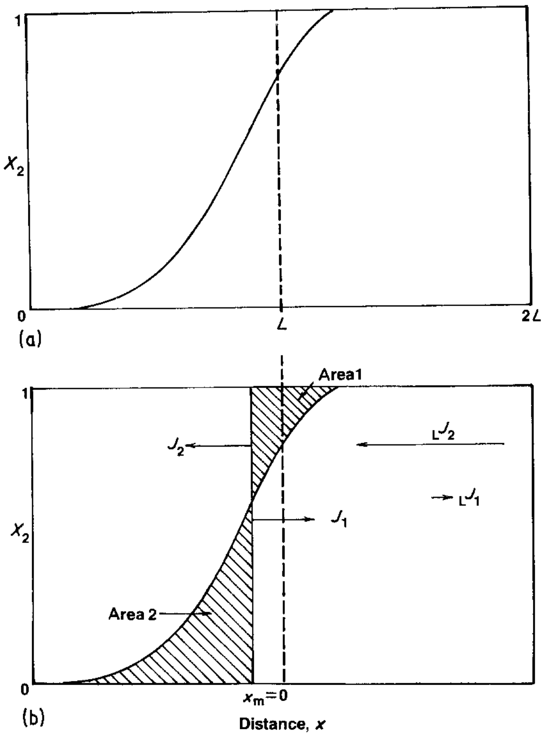

Figure 2 (a) The same experimental data as in Fig. 1 but plotted in terms of concentration in mole fraction X_2. (b) Location of the origin $x_m = 0$ of the molecular reference system on the diffusion curve of (a). Area 1 is not equal to Area 2. The fluxes J relative to the molecular reference system are compared schematically with the fluxes $_LJ$ relative to the lattice reference system.

terms of C_2 (Equation 17), and therefore to obtain the usual interdiffusion coefficient $\tilde{D}$ as a measure of diffusion.

The experimental data of Fig. 1a can alternatively be plotted in terms of mole fraction X_2 as shown in Fig. 2a. Since the molecular reference system is defined in terms of the X_i (Equation 10), it is convenient in this case to use fluxes referred to the molecular reference system

$$J_1 = C_1(v_1 - \omega_m) \quad \text{and} \quad J_2 = C_2(v_2 - \omega_m) \tag{19}$$

The relation between the two fluxes in this case can be obtained from Equation 14 with the aid of the relations

$$X_1 = C_1\bar{V} \quad \text{and} \quad X_2 = C_2\bar{V} \tag{20}$$

where $\bar{V}$ is the (total) molar volume of the solid solution. The result is

$$J_1 = -J_2 \tag{21}$$

Thus, equal numbers of atoms of Components 1 and 2 diffuse in opposite directions across reference planes in the molecular reference system. This relation between the two fluxes is shown schematically in Fig. 2b for the reference plane at $x_m = 0$ in the molecular reference system. The number of atoms of Metal 2 that crossed this reference plane to the left must equal the number of atoms of Metal 1 that crossed this reference plane in the opposite direction. The location of this reference plane can be determined more easily on a plot of the diffusion curve in terms of the concentration unit C_2 (Fig. 1b), since the areas corresponding to Area 1 and Area 2 in Fig. 2b are then equal and can be shown to contain equal numbers of atoms of Components 1 and 2, respectively. Because in our example Atom 1 has twice the volume of Atom 2 (because $\bar{V}_1 = 2\bar{V}_2$), the origin in Fig. 2b does *not* coincide with the midpoint L of the specimen in Fig. 2a, but instead continuously moves away from the midpoint with increasing time of diffusion.

It is not difficult to reconcile the equal conventional fluxes, $J_1 = -J_2$ (and the single D value discussed below), with the fact that Atoms 1 and 2 are "really" diffusing at different rates, as shown by the ratio of their intrinsic diffusion coefficients, $_fD_2/_fD_1 = 5$. The "real" fluxes shown schematically in Fig. 2b are those relative to the Kirkendall interface (Equation 44, Section 3) and represent the result of actual jumping (interchange with vacancies) of Atoms 1 and 2. A conventional flux is the sum of a component caused by atomic jumping plus a convective component (bulk movement of the volume elements as a whole) caused by a combination of (a) differences in atomic volume and (b) the Kirkendall shift. For clarity in the present illustrative example, values of $\bar{V}_i$ and $_fD_i$ have been chosen to cause the two contributions to convection to act in opposite directions.

The usual mutual diffusion coefficient $\tilde{D}$ was defined by Equation 17 in terms of the Fick reference system. Consequently, when the first Fick law is written in terms of the molecular reference system

$$J_2 = -D_m\frac{dC_2}{dx} \tag{22}$$

the diffusion coefficient D_m must have a different value than $\tilde{D}$. The reasoning is the following.

Even though the Cartesian coordinate system x_m (fixed in the molecular reference system) is moving relative to the corresponding Fick system x_f, the concentration gradients are equal [12], i.e. $dC_2/dx_m = dC_2/dx_f$. Consequently, the concentration gradients in Equations 17 and 22 are equal. The fluxes ${}_fJ_2$ and J_2, however, are unequal as can be seen from a comparison of Equations 15 and 19. Therefore, $\tilde{D}$ and D_m must be unequal. The relation between them can be determined with the aid of Equations 15 and 19, since

$$ {}_fJ_2 = -\tilde{D}\frac{dC_2}{dx} = C_2(v_2 - \omega_f) \quad (23) $$

and

$$ J_2 = -D_m\frac{dC_2}{dx} = C_2(v_2 - \omega_m) \quad (24) $$

When the values of ω_f from Equation 12 and of ω_m from Equation 10 are substituted in Equations 23 and 24, division of Equation 24 by Equation 23 leads to the relation

$$ D_m = \frac{\bar{V}}{\bar{V}_1}\tilde{D} \quad (25) $$

Substitution of Equation 25 in Equation 22 gives the form of the first Fick law for the molecular reference system in terms of $\tilde{D}$:

$$ J_2 = -\frac{\tilde{D}\bar{V}}{\bar{V}_1}\frac{dC_2}{dx} \quad (26) $$

Alternatively, using the relation

$$ \frac{dC_2}{dx} = \frac{\bar{V}_1}{\bar{V}^2}\frac{dX_2}{dx} \quad (27) $$

we can rewrite Equation 26 in terms of a concentration gradient in mole fraction,

$$ J_2 = -\frac{\tilde{D}}{\bar{V}}\frac{dX_2}{dx} \quad (28) $$

Equations 26 and 28 are valid for variable molar volumes. Just as the Fick reference system is connected with concentrations in moles per unit volume C_i, the molecular reference system is connected with mole fractions X_i. For this reason the form of Fick's law given by Equation 28 is usually convenient for calculating J_i fluxes.

Equations 17 and 22 represent Fick's law written for two different conventional reference systems. Since D_m is not equal to $\tilde{D}$, evidently the interdiffusion coefficient is *not* invariant relative to such a coordinate transformation. This fact does not agree with the central idea of a related series of paper in 1965 and 1966 by various authors [5, 6]. These authors proposed the concept of an "invariant" for binary interdiffusion

$$ \tilde{D} = C_1\bar{V}_1\,{}_fD_2 + C_2\bar{V}_2\,{}_fD_1 \quad (29) $$

where $\tilde{D}$ is the ordinary interdiffusion (or mutual) diffusion coefficient, and ${}_fD_1$ and ${}_fD_2$ are intrinsic diffusion coefficients of Components 1 and 2. This relation among the three D values was thought to remain the same for any choice of reference frame and to be valid for variable partial molar volumes. Since $C_1\bar{V}_1$ and $C_2\bar{V}_2$ are the *volume* fractions of Components 1 and 2, Equation 29 does not agree with Darken's well-known relation

$$ \tilde{D} = X_1D_2 + X_2D_1 \quad (30) $$

where X_1 and X_2 are *atom* fractions. Unfortunately the erroneous concept of an invariant for diffusion has been used in related work by other authors [7, 9] and in this way continues to influence present research results [13]. In fact, the relation of Equation 29 is merely the correct relation between $\tilde{D}$ and the intrinsic diffusion coefficients when the latter are defined by analogy with Equation 17, giving the ${}_fD_i$ coefficients. Equation 30, on the other hand, is for use with intrinsic coefficients defined by analogy with Equation 28, giving the D_i coefficients. This point is discussed in detail in Section 3.

The analysis by Stark [6] of the "invariant" has been widely quoted, and for this reason the erroneous features of his analysis will be explained here. It is well known and has been clearly described by Haase [11] that the velocities v_1 and v_2 in Equation 7 must be measured relative to some reference velocity. In view of the fact that Stark chooses ${}_fD_1$ and ${}_fD_2$ to be intrinsic diffusion coefficients, he automatically chooses the reference velocity to be that of the lattice (Kirkendall) reference system. In particular for the composition at the Kirkendall interface the relations in Equation 7 have the operational meaning

$$ {}_KJ_1 = C_1(v_1 - v_K) $$

and

$$ {}_KJ_2 = C_2(v_2 - v_K) \quad (31) $$

where v_K is the velocity of the Kirkendall interface. These relations state that the fluxes of Components 1 and 2 are measured as the number of moles that cross the Kirdendall interface, in agreement with the meaning attached to the intrinsic diffusion coefficients ${}_{\mathrm{f}}D_1$ and ${}_{\mathrm{f}}D_2$.

Stark next obtains the difference

$$\frac{{}_{\mathrm{K}}J_1}{C_1} - \frac{{}_{\mathrm{K}}J_2}{C_2} = (v_1 - v_{\mathrm{K}}) - (v_2 - v_{\mathrm{K}})$$
$$= v_1 - v_2 \qquad (32)$$

and attempts to show that

$$v_1 - v_2 = v'_1 - v'_2 \qquad (33)$$

under an arbitrary transformation of coordinates. Obviously he does not mean a transformation in scale (such as from centimetres to inches) since a scale factor (such as 2.54) is then introduced. If he means the v_{K} can be changed to a different value v'_{K}, then he is requiring a change in the diffusional characterisitcs of the system and both ${}_{\mathrm{K}}J_1$ and ${}_{\mathrm{K}}J_2$ must change to different values, ${}_{\mathrm{K}}J'_1$ and ${}_{\mathrm{K}}J'_2$. A change of this sort occurs in going from the Cu–Ni system, for example, to the Cu–Zn systems, but it is not considered to be a transformation of coordinates.

The next step in Stark's analysis is to define two diffusion coefficients by the equations

$$J_1 = -D_1\frac{\mathrm{d}C_1}{\mathrm{d}x} \quad \text{and} \quad J_2 = -D_2\frac{\mathrm{d}C_2}{\mathrm{d}x} \qquad (34)$$

and to state that this definition is valid for any coordinate system. In fact, as shown above in Equation 31, $J_1 = {}_{\mathrm{K}}J_1$ and $J_2 = {}_{\mathrm{K}}J_2$ and thus they are determined for one specific reference frame, the lattice coordinates. Stark's definition of intrinsic diffusion coefficients in Equation 34 is further restricted by the fact that he chose the analogue of Equation 17 rather than the analogue of Equation 28. Consequently, his coefficients must be written ${}_{\mathrm{f}}D_1$ and ${}_{\mathrm{f}}D_2$ to distinguish them from the more rational D_1 and D_2 employed in Equation 30.

The irrationality of ${}_{\mathrm{f}}D_1$ and ${}_{\mathrm{f}}D_2$ can be appreciated when one recalls that the Kirkendall effect is intended to measure the difference in the number of atoms of Metal 1 and Metal 2 that diffuse across a plane fixed in the lattice (the Kirkendall interface). Consider a case in which $J_1 = -J_2$, so that the Kirkendall effect is zero. Because

$$\frac{\mathrm{d}C_1}{\mathrm{d}x} = -\frac{\bar{V}_2}{\bar{V}_1}\frac{\mathrm{d}C_2}{\mathrm{d}x} \qquad (35)$$

${}_{\mathrm{f}}D_1$ is *not* equal to ${}_{\mathrm{f}}D_2$ in Equation 34; instead

$${}_{\mathrm{f}}D_1 = \frac{\bar{V}_1}{\bar{V}_2}\,{}_{\mathrm{f}}D_2 \qquad (36)$$

in the absence of a Kirkendall effect. On the other hand, if the analogue of Equation 28 is employed, the resulting intrinsic diffusion coefficients (D_1 and D_2) are equal if $J_1 = -J_2$.

In summary, the correct interpretation of Stark's analysis shows that his final result (Equation 29), rather than being a useful invariant, is simply the fixed relation between the generally accepted interdiffusion coefficient $\tilde{D}$ and a type of intrinsic coefficient (${}_{\mathrm{f}}D_1$ and ${}_{\mathrm{f}}D_2$) defined in an unsatisfactory manner. A more useful relation of the same type is Equation 30, which is identical with the well-known Darken relation for the case of equal, constant partial molar volumes.

Carl Wagner was influenced by Stark's analysis in his treatment of interdiffusion [7]. Wagner, however, did not introduce intrinsic coefficients but dealt only with a single interdiffusion coefficient $\tilde{D}$, determined by two different atomic velocities v or fluxes J:

$$\tilde{D} = \frac{X_1X_2(v_1 - v_2)}{\mathrm{d}X_2/\mathrm{d}x} = \frac{\bar{V}(X_2J_1 - X_1J_2)}{\mathrm{d}X_2/\mathrm{d}x} \qquad (37)$$

Since there is only one independent coefficient ($\tilde{D}$) in the absence of data on the motion of markers, the two coefficients ${}_{\mathrm{C}}D_1$ and ${}_{\mathrm{C}}D_2$ associated with J_1 and J_2 (or with v_1 and v_2) are interrelated in a manner that depends on the choice of conventional (subscript C) reference system. Because Wagner set $J_1 = -J_2$ (by his determination of the Matano interface) and used Equation 17 for the first Fick law, it follows that

$${}_{\mathrm{C}}D_1 = \frac{\bar{V}_1}{\bar{V}_2}\,{}_{\mathrm{C}}D_2 \qquad (38)$$

Thus, Wagner's relation (Equation 37) is more complex than necessary because of an inconvenient choice of reference system. By use of Equation 28 the same physical meaning is given by the simpler expression

$$\tilde{D} = \frac{\bar{V}J_1}{\mathrm{d}X_2/\mathrm{d}x} \tag{39}$$

This result can also be obtained from Equation 37, since $X_2 = 1 - X_1$ and $J_2 = -J_1$.

The difference between the use of Equations 39 and 37 is this: in the first case $\tilde{D}$ is determined directly by Equation 39, whereas in the second case $\tilde{D}$ is determined through the intermediate relation

$$\tilde{D} = C_1\bar{V}_1\,{}_\mathrm{C}D_2 + C_2\bar{V}_2\,{}_\mathrm{C}D_1 \tag{40}$$

when Equation 37 is employed. In addition to this unnecessary complexity accompanying the use of ${}_\mathrm{C}D_1$ and ${}_\mathrm{C}D_2$, there is the possibility of the serious error dicussed above in connection with Equation 1. Sauer and Freise [4] made this error and employed the form of the first Fick law appropriate for the Fick reference system (Equation 1), although they employed the molecular reference system (by virtue of their method for determining the Matano interface). Consequently, Sauer and Freise concluded incorrectly that there are two different Matano interfaces which move further apart as diffusion proceeds. As shown by van Loo [9], Balluff's treatment [3] is equivalent to that of Sauer and Freise [4]. Thus, all of the previous treatments based on the use of ordinary Cartesian coordinates are similar and suffer from two defects: (a) unnecessary complexity (Equation 40); and (b) likelihood of error in applying $\tilde{D}$.

Cohen *et al.* [2] devised a treatment based on a special coordinate ξ, such that

$$\mathrm{d}\xi = \mathrm{d}x/\bar{V} \tag{41}$$

They employed the molecular reference system and obtained for the second Fick law

$$\frac{\partial X_1}{\partial t} = \frac{\partial}{\partial \xi}\left(D'\frac{\partial X_1}{\partial \xi}\right) \tag{42}$$

where D' is the coefficient appropriate for use with the special coordinates. Son and Sano [10] have shown that the relation

$$D' = \tilde{D}/\bar{V}^2 \tag{43}$$

is general, and that a restriction to dilute solutions [2] is unecessary. With the use of Equations 41 and 43, Equation 42 becomes identical with Equation 69 (Section 5). In view of the convenience of Cartesian coordinates, there is no reason to use Equation 42 with its special coordinates since Equation 69 also has a simple form.

3. Lattice reference system

The conventional reference velocities ω_m and ω_f considered in Section 2 were obtained as weighted averages (Equations 10 and 12), of the diffusion velocities v_1 and v_2 of the two components. A conventional velocity need not correspond to any experimentally observable feature of the diffusion system. In contrast, a lattice reference velocity, $\omega = \omega_\mathrm{L}$, is basically obtained from experimental measurements of motion of the crystal lattice. Because no relation between v_1 and v_2 is generally involved, the two diffusion fluxes defined by Equation 13 are now independent;

$$ {}_\mathrm{L}J_1 = C_1(v_1 - \omega_\mathrm{L})$$

and

$$ {}_\mathrm{L}J_2 = C_2(v_2 - \omega_\mathrm{L}) \tag{44}$$

(In the treatment beginning with Equation 31 and also in the work of Guy and Oikawa [1], the notation v_K and ${}_\mathrm{K}J_i$ was used for the quantities ω_L and ${}_\mathrm{L}J_i$. The present notation is more general, since Kirkendall (subscript K) markers represent only one of various techniques for obtaining information on the velocity of the crystal lattice.) Since two independent diffusion fluxes are given by Equation 44, it follows that there should be two independent diffusion coefficients. These coefficients can be defined in significantly different ways, by analogy with Equations 17 or 28. We will first consider the results obtained with Equation 17.

Because Equation 17 is associated with the Fick (subscript f) reference system, the analogous equations define intrinsic diffusion coefficients ${}_\mathrm{f}D_i$ by the following form of the first Fick law;

$$ {}_\mathrm{L}J_1 = -\,{}_\mathrm{f}D_1\frac{\mathrm{d}C_1}{\mathrm{d}x} \quad\text{and}\quad {}_\mathrm{L}J_2 = -\,{}_\mathrm{f}D_2\frac{\mathrm{d}C_2}{\mathrm{d}x} \tag{45}$$

The relation between these two fluxes can be determined with the aid of Equation 6 and is found to be

$$ {}_\mathrm{L}J_1 = -\frac{\bar{V}_2\,{}_\mathrm{f}D_1}{\bar{V}_1\,{}_\mathrm{f}D_2}\,{}_\mathrm{L}J_2 \tag{46}$$

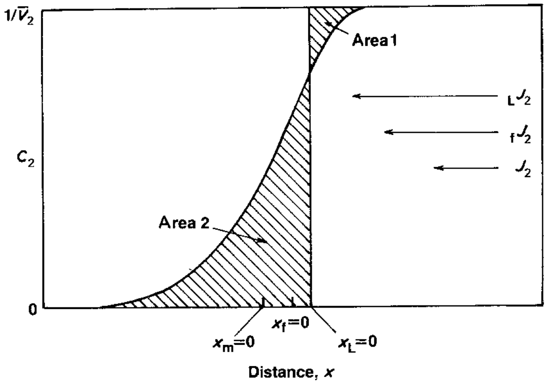

Figure 3 Schematic illustration of the position of the Kirkendall interface $x_\mathrm{L} = 0$ on the diffusion curve of Fig. 1. The positions of the origins of the two conventional reference systems are shown for comparison. The relative magnitudes of the three types of fluxes in the volume element at the composition of the Kirkendall interface are indicated by the length of the arrows.

Fig. 3 shows schematically how the Kirkendall interface is related to the diffusion curve of Fig. 1. In this case Areas 1 and 2 are in the ratio $\bar{V}_2\,{}_\mathrm{f}D_1/\bar{V}_1\,{}_\mathrm{f}D_2$ or 1/10. The positions of the origins of the two conventional reference systems are also indicated.

Just as $\tilde{D}$ is adequate for describing a given diffusion curve in terms of the Fick reference system, so also is the pair ${}_\mathrm{f}D_1$ and ${}_\mathrm{f}D_2$ an equivalent adequate means for describing the same diffusion curve. In view of this equivalence of $\tilde{D}$ to ${}_\mathrm{f}D_1$ with ${}_\mathrm{f}D_2$, a relation must exist among these three coefficients. The following procedure can be used to establish the relation that exists between the two lattice fluxes and the equivalent flux in the Fick reference system. Employing Equations 12 and 5, we can manipulate Equations 15 and 44 as follows:

$$\bar{V}_2\,{}_\mathrm{f}J_2 = \bar{V}_2 C_2(v_2 - \omega_\mathrm{f})$$

$$= C_1\bar{V}_1 C_2\bar{V}_2(v_2 - v_1) \quad (47)$$

$$\bar{V}_1\bar{V}_2 C_2\,{}_\mathrm{L}J_1 = \bar{V}_1\bar{V}_2 C_1 C_2(v_1 - \omega_\mathrm{L}) \quad (48)$$

$$\bar{V}_1\bar{V}_2 C_1\,{}_\mathrm{L}J_2 = \bar{V}_1\bar{V}_2 C_1 C_2(v_2 - \omega_\mathrm{L}) \quad (49)$$

When Equation 48 is subtracted from Equation 49 and the difference is compared with Equation 47, the result is

$$\bar{V}_1(C_1\,{}_\mathrm{L}J_2 - C_2\,{}_\mathrm{L}J_1) = {}_\mathrm{f}J_2 \quad (50)$$

as the desired relation among the fluxes. The corresponding relation among the diffusion coefficients is obtained by substituting Equations 17 and 45 into Equation 50, to give

$$\tilde{D} = C_1\bar{V}_1\,{}_\mathrm{f}D_2 + C_2\bar{V}_2\,{}_\mathrm{f}D_1 \quad (51)$$

This relation is the so-called "invariant" (Equation 29) discussed above, and depends on the use of Equation 17 for the first Fick law.

If Equation 28 is used as the first Fick law, the two parts of Equation 45 take the form

$${}_\mathrm{L}J_1 = -\frac{D_1}{\bar{V}}\frac{\mathrm{d}X_1}{\mathrm{d}x}$$

and $${}_\mathrm{L}J_2 = -\frac{D_2}{\bar{V}}\frac{\mathrm{d}X_2}{\mathrm{d}x} \quad (52)$$

where D_1 and D_2 are the intrinsic diffusion coefficients defined by these equations. These D_i values are related to the molecular reference system, but the "m" subscript is omitted for simplicity. A derivation analogous to that of Equations 47 to 51 can be made for the molecular reference system using Equation 52 in place of Equation 45. The result is Darken's relation (Equation 30). Both Equations 51 and 30 are valid for variable partial molar volumes.

4. Absolute diffusion velocities in metals

In Section 2, conventional reference systems were treated in terms of a reference velocity ω (Equation 8) that is a weighted average of the diffusion velocities v_i of the two components. In this case only the difference in velocity $(v_i - \omega)$ has physical significance [11]. If, on the other hand, the lattice reference system is employed, it will now be shown that absolute values of diffusion velocity can be determined and employed in calculations. This means that equations of the form

$$J_i = v_i C_i \quad (53)$$

can be employed.

To demonstrate the nature of absolute diffusion velocities, only the simplest case of binary diffusion need be considered; namely, interdiffusion of two pure metals, Metals 1 and 2, that form a complete series of solid solutions under the conditions of diffusion. After diffusion, the intial plane that separated the two metals can be seen microscopically as a faint line of oxide particles forming the Kirkendall interface. Chemical analysis can determine the total quantity Q_i of Metal i that diffused across the Kirkendall interface and entered the other metal. For the composition C_i^{K} of the Kirkendall interface, the value of v_i can then be determined by the relation

$$\int_0^{\tau} J_i \mathrm{d}t = \frac{Q_i}{A} = \int_0^{\tau} v_i C_i^{\mathrm{K}} \mathrm{d}t \qquad (54)$$

where A is the cross-sectional area of the specimen and τ is the time of diffusion. Since the Kirkendall interface shifts relative to a fiducial reference plane (such as an undiffused plane in the specimen) at a rate proportional to $1/\tau^{1/2}$,

$$v_i = \frac{M_i}{\tau^{1/2}} \qquad (55)$$

where M_i is a constant for a given diffusion specimen. The composition C_i^{K} at the Kirkendall interface remains constant, and therefore when the value for v_i given by Equation 55 is substituted in Equation 54, definite integration yields the relation

$$C_i^{\mathrm{K}} M_i = \frac{Q_i}{2A\tau^{1/2}} \qquad (56)$$

Substitution of Equation 56 in Equation 55 gives the desired expression for the absolute velocity of component i:

$$v_i = \frac{Q_i}{2C_i^{\mathrm{K}} A\tau} \qquad (57)$$

Although the velocities v_i and therefore the fluxes J_i have absolute values, the magnitudes of the corresponding diffusion coefficients D_i depend on the choice of the definition of Fick's first law as discussed in Section 3. The two common definitions (Equations 17 and 28) lead to the alternative expressions for the intrinsic diffusion coefficient

$$J_i = -{}_{\mathrm{f}}D_i \frac{\mathrm{d}C_i}{\mathrm{d}x} \qquad (58)$$

and

$$J_i = -\frac{D_i}{\bar{V}} \frac{\mathrm{d}X_i}{\mathrm{d}x} \qquad (59)$$

The advantages of the D_i defined by Equation 59 were discussed above in connection with Equation 36.

The intrinsic diffusion coefficient D_i can be expressed in terms of experimental quantities in the following manner. Use of the variable $\lambda = x/\tau^{1/2}$ permits writing Equation 59 in the form

$$J_i = -\frac{D_i}{\bar{V}\tau^{1/2}} \frac{\mathrm{d}X_i}{\mathrm{d}\lambda} \qquad (60)$$

For a given value of X_i, $\mathrm{d}X_i/\mathrm{d}\lambda$ has a constant value. Therefore, for the value X_i at the Kirkendall interface it follows from Equations 53, 57 and 60 that

$$D_i = -\frac{Q_i \bar{V}}{2A\tau^{1/2}} \frac{\mathrm{d}\lambda}{\mathrm{d}X_i} = -\frac{Q_i \bar{V}}{2A\tau} \frac{\mathrm{d}x}{\mathrm{d}X_i} \qquad (61)$$

where $\mathrm{d}X_i/\mathrm{d}x$ is the concentration gradient at the Kirkendall interface after diffusion for the time τ. Equation 61 permits experimental determination of the value of the intrinsic coefficient D_i, for use in the first Fick law given by Equation 59.

5. The second Fick law

An important problem in diffusion theory is the calculation of $\tilde{D}$ from an experimentally determined diffusion curve for a binary alloy system in which appreciable changes in volume occur. The starting point for such an analysis is a definition of $\tilde{D}$, but fortunately there is general consensus that $\tilde{D}$ is defined by Equation 17; that is, relative to the Fick reference system and with concentration C_2 in moles per unit volume. As shown by Equation 16, the origin $x_{\mathrm{f}} = 0$ of the Fick reference system remains fixed with respect to the ends of the specimen if the partial molar volumes $\bar{V}_1$ and $\bar{V}_2$ are constant. If $\bar{V}_1$ and $\bar{V}_2$ are functions of concentration, however, the overall length of the specimen will change (Fig. 4) and in general $x_{\mathrm{f}} = 0$ will continuously shift away from the position $x_{\mathrm{e}} = 0$ (fixed with respect to an end of the specimen) which it occupied at the start of the diffusion process. If $\tilde{D}$ is to retain a meaning consistent with that for simpler cases, it must be defined relative to a conventional reference system, specified for example by $x_{\mathrm{f}} = 0$ or $x_{\mathrm{m}} = 0$ in Fig. 4. The disadvantages of the choice of $x_{\mathrm{e}} = 0$ or of $x_{\mathrm{f}} = 0$ have been discussed in Section 2.

Not only does the molecular reference system have advantages relative to ease of analysis, but its origin ($x_{\mathrm{m}} = 0$) is easily located on an experimental diffusion curve. Because equal numbers of atoms of Metals 1 and 2 have crossed a molecular reference plane, the plane at $x_{\mathrm{m}} = 0$ divides the diffusion curve into two parts such that Area 1 and 2 in Fig. 4 are equal. For this

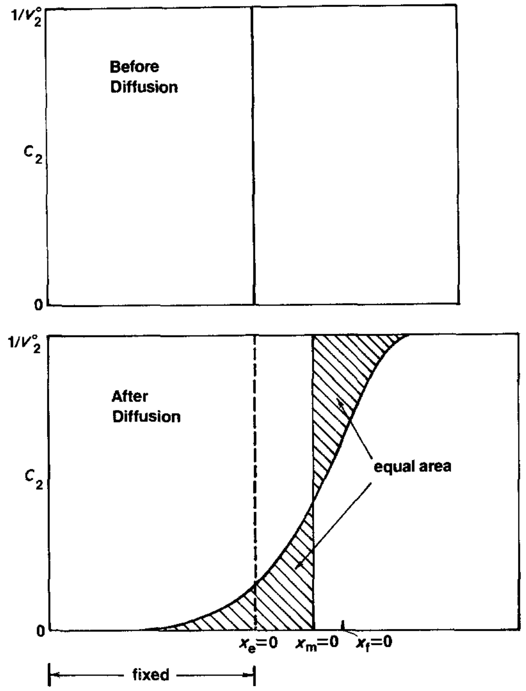

Figure 4 Schematic illustrations of a fixed reference system x_e, and of two conventional reference systems x_f and x_m, in the case of volume changes that produce expansion in a diffusion couples. V_2^0 is the molar volume of pure Metal 2.

choice of reference system, the first Fick law can be written in terms of mole fraction X_1 in the form given by Equation 28. The conversion of this form of the first Fick law into a conventional form of the second Fick law will now be considered.

The derivation of the second Fick law must take account of two contributions to the rate of change of composition with time, $\partial C_1/\partial t$. The first is the usual accumulation of Component 1 per second in a volume element of thickness $\mathrm{d}x$ and of unit area;

$$\frac{\partial}{\partial x}(-J_1)\,\mathrm{d}x = \frac{\partial}{\partial x}\left(\frac{\tilde{D}}{\bar{V}}\frac{\partial X_1}{\partial x}\right)\mathrm{d}x \qquad (62)$$

The second contribution arises from the loss of Component 1 from the volume element because of expansion due to the effects associated with changes in the partial molar volumes. The latter contribution can be determined as follows, starting with the standard expression for the total molar volume:

$$\bar{V} = X_1\bar{V}_1 + X_2\bar{V}_2 \qquad (63)$$

The rate of change of $\bar{V}$ is

$$\begin{aligned}\frac{\partial \bar{V}}{\partial t} &= \bar{V}_1\frac{\partial X_1}{\partial t} + \bar{V}_2\frac{\partial X_2}{\partial t} + X_1\frac{\partial \bar{V}_1}{\partial t} + X_2\frac{\partial \bar{V}_2}{\partial t} \\ &= (\bar{V}_1 - \bar{V}_2)\frac{\partial X_1}{\partial t} \qquad (64)\end{aligned}$$

since $X_1\,\mathrm{d}\bar{V}_1 + X_2\,\mathrm{d}\bar{V}_2 = 0$. If the entire change in volume occurs as an expansion in the x direction, the velocity of separation of the two molecular reference planes separated by the distance $\mathrm{d}x$ is

$$v = \frac{(\bar{V}_1 - \bar{V}_2)}{\bar{V}}\frac{\partial X_1}{\partial t}\,\mathrm{d}x \qquad (65)$$

The amount vC_1 of Component 1 is removed from the volume element as a result of the expansion in question.

When Equations 62 and 65 are employed to determine $\partial C_1/\partial t$ the result is

$$\frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x}\left(\frac{\tilde{D}}{\bar{V}}\frac{\partial X_1}{\partial x}\right) - \frac{C_1(\bar{V}_1 - \bar{V}_2)}{\bar{V}}\frac{\partial X_1}{\partial t} \qquad (66)$$

Using the relation $X_1 = C_1\bar{V}$,

$$\frac{\partial C_1}{\partial t} = \frac{1}{\bar{V}}\frac{\partial X_1}{\partial t} - \frac{X_1}{\bar{V}^2}\frac{\partial \bar{V}}{\partial t} \qquad (67)$$

Substitution of the value of $\partial\bar{V}/\partial t$ from Equation 64 gives

$$\frac{\partial C_1}{\partial t} = \frac{1}{\bar{V}}\left[1 - \frac{X_1(\bar{V}_1 - \bar{V}_2)}{\bar{V}}\right]\frac{\partial X_1}{\partial t} \qquad (68)$$

When this expression is employed in Equation 66, the final result is

$$\frac{1}{\bar{V}}\frac{\partial X_1}{\partial t} = \frac{\partial}{\partial x}\left(\frac{\tilde{D}}{\bar{V}}\frac{\partial X_1}{\partial x}\right) \qquad (69)$$

This relatively simple form of the second Fick law has not previously been reported in the literature.

For the special case in which $\bar{V}_1 = \bar{V}_2$, Equation 69 reduces to the usual equation

$$\frac{\partial X_1}{\partial t} = \frac{\partial}{\partial x}\left(\tilde{D}\frac{\partial X_1}{\partial x}\right) \qquad (70)$$

For the special case of constant but unequal values of $\bar{V}_1$ and $\bar{V}_2$, however, Equation 69 must be used in essentially its complete form since $\bar{V}$ is then a linear function of X_1. A simpler procedure in this case is to use volume fraction as the unit of concentration [14] since the second Fick law then has the form of Equation 70. The appropriate interface for use with the Boltzmann–Matano method in this case divides the diffusion curve into two unequal areas in the ratio $\bar{V}_2/\bar{V}_1$. In contrast, the origin of the molecular reference system divides the diffusion curve into two equal areas.

The actual evaluation of $\tilde{D}$ from the experimental data of a diffusion curve by means of Equation 69 can be done either graphically or with the aid of a suitable computer program. In either case the most convenient procedure is that given by Equation 9 in den Broeder's paper [8], since the position coordinate of the Matano interface need not be detemined explicitly in this method.

6. Discussion

Anyone who has tried to include the effects of variable molar volumes in an analysis of diffusion (or any other phenomenon) can testify to the perplexing difficulties that are encountered. These difficulties have even led to such misleading treatments in the literature as the "invariant" discussed in Section 2. The key to the resolution of these difficulties is surprisingly elementary; namely, a proper use of reference planes. For example, even though the variation in molar volume causes a specimen to increase in length, a reliable point in the specimen is furnished by the origin of the molecular reference system. An immediate consequence of the availability of this reference point is the feasibility of using ordinary Cartesian coordinates for an analysis.

The use of Equation 28 as the analogue for defining the intrinsic diffusion coefficients has the advantages discussed in Section 2. The basic correctness of this procedure, moreover, is shown by the fact that the same definition is preferred for the general treatments of nonequilibrium thermodynamics [15] and for analyses of diffusion in gases [16].

The present demonstration of absolute diffusion velocities has two significant aspects. First, it gives an example of a system in which a reference velocity is not essential. Previously [11], even for systems in which Kirkendall shifts had been measured, a lattice reference velocity was employed in the analysis. Second, although it was known that intrinsic diffusion coefficients could be determined from the (absolute) fluxes crossing a Kirkendall interface, it was not recognized that these coefficients could have two different values, ${}_{\mathrm{F}}D_i$ or D_i, depending on the choice of reference system (Fick or molecular) for the interdiffusion coefficient.

Acknowledgements

Acknowledgement is gratefully made of the important contributions to this paper made by Professor R. Haase (Technical University, Aachen, Germany) during his visit to the University of Florida in 1975. Professors R. T. De Hoff, H. B. Huntington and J. P. Stark have aided greatly by their comments and suggestions.

References

1. A. G. GUY and H. OIKAWA, *J. Non-Equilib. Thermodyn.* **8** (1983) 159.
2. M. COHEN, C. WAGNER and J. E. REYNOLDS, *Trans. AIME* **197** (1953) 1534.
3. R. W. BALLUFFI, *Acta Metall.* **8** (1960) 871.
4. F. SAUER and V. FREISE, *Z. Electrochem.* **66** (1962) 353.
5. L. E. TRIMBLE, D. FINN and A. COSGAREA, *Acta Metall.* **13** (1965) 501.
6. J. P. STARK, *ibid.* **14** (1966) 228.
7. C. WAGNER, *ibid.* **17** (1969) 99.
8. F. J. A. DEN BROEDER, *Scripta Metall.* **3** (1969) 321.
9. F. J. J. VAN LOO, *Acta Metall.* **18** (1970) 1107.
10. P. SON and T. SANO, *Scripta Metall.* **8** (1974) 85.
11. R. HAASE, "Thermodynamics of Irreversible Processes" (Addison-Wesley, Reading, Massachusetts, 1969) p.218.
12. P. G. SHEWMON, "Diffusion in Solids" (McGraw-Hill, New York, 1963) p.119.
13. T. HEUMANN and T. ROTTWINKEL, *J. Nuclear Mater.* **69/70** (1978) 567.
14. A. G. GUY, R. T. DE HOFF and C. B. SMITH, *ASM Trans. Quart.* **61** (1968) 314.
15. G. J. HOOYMAN, H. HOLTAN, P. MAZUR and S. R. DE GROOT, *Physica* **19** (1953) 1095.
16. E. A. MASON, R. J. MUNN and F. J. SMITH, *Adv. At. Molec. Phys.* **2** (1966) 36.

*Received 28 February
and accepted 18 December 1984*