

10-1975

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REFERENCE FRAMES AND DIFFUSION COEFFICIENTS

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ABSTRACT. Diffusion coefficients are empirical constants that express linear relationships between fluxes of chemical components and gradients in composition variables. Component fluxes must be measured with respect to some particular frame of reference, so diffusion coefficients depend on the choice of reference frame as well as the choice of composition gradient. Reference frames based on a mean velocity of all the components, such as the velocity of the center of mass, are particularly convenient, for results obtained using different mean velocity frames may be readily interrelated. Diffusion data is best presented in terms of "standard" diffusion coefficients, D°_{ij} , based on the mean volume reference frame. The continuity equation for a specific reference frame R is given by

$$\left(\frac{\partial \rho_i}{\partial t} \right)_{P,T,x} = - \left[\frac{\partial}{\partial x} \left(J_i^R + \rho_i \bar{v}^{RL} \right) \right]_{P,T,t}$$

where \bar{v}^{RL} is the local velocity of reference frame R with respect to a fixed point not affected by the diffusion process. If there is a volume change during a binary diffusion process in a single crystal, the continuity equation may be solved using a modified distance scale based on appropriate lattice translations in the crystal of interest. Interdiffusion behavior may be predicted on the basis of isotopic self-diffusion measurements; the exact relationship utilized for ionic crystals is not identical to Darken's equation for metallic crystals.

1. INTRODUCTION

The process of diffusion involves the net transfer of atoms due to random thermal motions of atoms initially in a non-random distribution and/or to non-random thermal motions of atoms subject to a driving force. In order to describe and quantify this net movement of atoms, macroscopic measurements must be made with respect to some specific frame of reference, usually consisting of a set of identifiable points. In principle, any set of reference points may be used as long as *all* measurements are made with respect to the same set. In practice, however, it may be inconvenient or impossible to use the same reference frame for all measurements and applications. Since different reference frames lead to different descriptions of diffusion and, therefore, to different diffusion coefficients, it is wise to select for common usage those reference frames that may be readily interrelated. For these reasons, an understanding of the various ways to describe diffusion and to define diffusion coefficients is a prerequisite to the discussion of any diffusion data or diffusion related process.

Extensive discussions of the subject of reference frames may be found in the chemical, physical, and metallurgical literature of the last 25 years. Outstanding papers include those by Darken (1948), Hartley and Crank (1949), Hooyman and others (1953), Hooyman (1956), Kirkwood and others (1960). An excellent summary may be found in a textbook by de Groot and Mazur (1962, p. 239 and following). Summaries may also be found in the texts by Fitts (1962, chap. 8) and Haase (1969, p. 271 and following). In spite of this rather thorough theoretical coverage of the subject, a unified treatment of reference frames is not available. The

several papers listed above utilize a number of different approaches, each designed to suit the problems most often encountered by the authors. In what follows I will reconsider the general topic of reference frames and show how the results of several of the listed authors are interrelated. I will then show how these results may be extended and modified to apply to problems of diffusion in common minerals.

Throughout this paper I consider only macroscopic or phenomenological descriptions of diffusion. Macroscopically, diffusion is manifested by local variations in the chemical composition of a physical system and may be explained, using simple mass balance considerations, in terms of the transfer of matter of definite chemical compositions into and/or out of the system. Hence, one describes diffusion as a motion of quantities of chemical components relative to some reference frame sufficient to produce the observed variations in chemical composition. The components used in the description need not correspond to any moving atomic or molecular species and may be selected on the basis of convenience (see Brady, 1975). For the purposes of this paper I assume that the components used are linearly independent and that the quantity of each component may be independently varied in the systems considered.

The equations presented in the following paragraphs are all for one-dimensional diffusion. To be complete, velocities, fluxes, forces, and diffusion coefficients should be given as tensor quantities. However, a one-dimensional representation is sufficient to convey the important concepts and simplifies the already cumbersome notation. The generalization to three dimensions is straightforward. The unit of quantity used throughout is moles of component i or gram-formula units of i . This choice of unit of quantity simplifies some of the discussion, particularly for the unit cell reference frame. Quantities that have meaning only if a reference frame is specified are written with superscripts to indicate a particular reference frame, R . The following is a list of the symbols used in the text.

NOTATION

a	— unit cell parameter (\AA)
$A = A^{+a}$	— cation with charge $+a$
$A_{ij}^{R,V}$	— parameters used to relate fluxes in reference frame R to fluxes in reference frame V (dimensionless) (3.11)
b	— unit cell parameter (\AA)
$B = B^{+b}$	— cation with charge $+b$
B_i^I	— mobility of component i ; velocity of component i with respect to the inert marker reference frame in response to a unit force ($\text{mole}\cdot\text{cm}^2/\text{cal}\cdot\text{sec}$) (7.1)
c	— unit cell parameter (\AA)
C_i	— any one composition variable for component i
$D_{ij}^{R,C}$	— practical diffusion coefficient; relates flux of component i with respect to reference frame R to gradient of component j given in terms of composition parameter C_j (3.6)

D°_{ij}	– “standard” practical diffusion coefficient; relates flux of component i with respect to the mean volume reference frame to gradient in molar density of component j (cm^2/sec) (3.11)
D_i^I	– inert marker diffusion coefficient defined in (6.13) and (6.10) (cm^2/sec)
G	– Gibbs free energy (cal)
i, j, k, l	– dummy subscripts used to represent various components
J_i^R	– flux of component i with respect to reference frame R (moles/ $\text{cm}^2\text{-sec}$) (2.4)
L_{ij}^R	– phenomenological diffusion coefficient; relates flux of component i with respect to reference frame R to the force produced by the chemical potential gradient of component j (mole 2 /cal-cm-sec) (3.1)
L_{ij}^R	– phenomenological diffusion coefficient; relates flux of component i to a set of independent forces given in (3.4) (mole 2 /cal-cm-sec)
M_i	– gram formula weight of component i (gm/mole)
n_i	– number of moles of component i
n_i^c	– number of moles of component i per unit cell
N_i	– $\frac{n_i}{\sum_{i=1}^n n_i}$; mole fraction of component i (dimensionless)
P	– pressure (bars)
q_i	– charge on species i (esu)
R	– gas constant (1.987 cal/mole-deg)
t	– time (sec)
T	– temperature ($^{\circ}\text{K}$)
v_i^L	– velocity of component i with respect to some laboratory frame L (cm/sec)
\bar{v}^{RL}	– a weighted average of the velocities of all components; velocity of mean velocity reference frame R (cm/sec) (2.2)
v_i^R	– velocity of component i with respect to mean velocity reference frame R (cm/sec) (2.3)
\bar{v}^{SR}	– velocity of reference frame S with respect to reference frame R (cm/sec) (2.6)
V	– volume (cm^3)
V_i	– $\left(\frac{\partial V}{\partial n_i}\right)_{P, T, n_j \neq i}$; partial molar volume (cm^3/mole)
\bar{V}	– $\frac{V}{\sum_{i=1}^n n_i}$; molar volume of a phase (cm^3/mole)
w_i^R	– weight given the velocity of component i in obtaining mean velocity \bar{v}^{RL} (dimensionless) (2.1)

x	— distance (cm)
$Z = Z^{-z}$	— anion or chemical component with charge $-z$
γ_i	— activity coefficient for component i (dimensionless)
δ_{ik}	— $\begin{cases} =0 & \text{if } i \neq k \\ =1 & \text{if } i = k \end{cases}$; Kronecker delta function (dimensionless)
μ_i	— $\left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_j \neq i}$; chemical potential per mole of component i (cal/mole)
ξ_{ik}^c	— modified distance parameter for reference frame R based on unit cell edge c (dimensionless) (5.1)
ρ_i	— molar density of component i (moles/cm ³)
ϕ	— electrical potential (cal/esu)

Superscripts

C	— any one composition variable
I	— inert marker reference frame (sec. 6)
K	— K th component reference frame (2.10)
L	— laboratory reference frame (sec. 2)
M	— mean mass reference frame (2.11)
N	— mean molar reference frame (2.8)
R	— any one reference frame
V	— mean volume reference frame (2.9)
*	— indicates that the value is given for a radioactive isotope

2. MEAN VELOCITY REFERENCE FRAMES

A great number of papers have been written on the general subject of diffusion that make no mention whatsoever of the frame of reference in which the diffusive velocities and fluxes discussed are to be measured. The authors of nearly all these papers tacitly assume that the diffusive fluxes and velocities they discuss are measured with respect to a single identifiable point. This is equivalent to using a reference frame based on a set of points, each of which remains in a fixed position relative to the others at all times. I shall call this type of reference frame the laboratory frame, L , for it is commonly used by experimentalists in the description of transport processes. For example, fluxes in solid interdiffusion experiments are given with respect to one end of the sample. Similarly, in liquid diffusion experiments, fluxes are measured with respect to the container that holds the liquid, sometimes called the "cell-fixed" reference frame.

Although laboratory reference frames have obvious practical advantages, their general utility is severely limited by their multiplicity. Indeed, there are potentially as many laboratory reference frames as there are laboratories or experimentalists, and results obtained using such frames may be difficult or impossible to compare. For example, two observers of a solid interdiffusion experiment might pick opposite ends of the diffusion couple as the origin of their laboratory frames. If there is an overall volume change during the diffusion experiment, the two labora-

tory frames chosen would move with respect to one another. This means that two observers of the same experiment would obtain different values for fluxes and velocities of the same components.

These difficulties may be eliminated by reporting motion with respect to a reference frame that is independent of the particular laboratory frame selected by an observer. Such a reference frame can be defined by some weighted average of the velocities of all the chemical components involved, such as the velocity of the center of mass. Whatever laboratory frame is used to measure individual velocities in a given experiment, the same result would be reported by all observers for component velocities relative to the center of mass. This approach has its foundations in classical mechanics and was introduced to describe multicomponent diffusion by Hooyma (1956). Following Hooyma's terminology, I shall call reference frames of this type "mean velocity" reference frames.

Let v_i^L be the velocity of component i as measured by any one observer with respect to any single laboratory frame L at one point in space and at one particular time. Operationally, v_i^L would be a weighted average of the velocities of all the particles that contain component i . Selecting a set of dimensionless weighting factors w_i^R , such as mass fraction, mole fraction, or volume fraction, normalized according to the criteria

$$\sum_{i=1}^n w_i^R = 1 \quad (2.1)$$

we may define an average or mean velocity, \bar{v}^{RL} , for the n components of a given system as

$$\bar{v}^{RL} \equiv \sum_{i=1}^n w_i^R v_i^L \quad (2.2)$$

where the superscript R refers to the reference frame defined by (2.1) and (2.2). Although the magnitude of v_i^L and of the mean velocity \bar{v}^{RL} may vary from observer to observer, the velocity v_i^R of component i with respect to the mean velocity

$$v_i^R \equiv (v_i^L - \bar{v}^{RL}) \quad (2.3)$$

will be the same for all observers. On this basis, then, we may define the flux, J_i^R , of component i with respect to mean velocity reference frame R as

$$J_i^R \equiv \rho_i v_i^R \quad (2.4)$$

where ρ_i is the molar density of i and where the flux, J_i^R , is given in units of moles of i per cm^2 per second. J_i^R will be the same for all observers of the same event.

Comparing equations (2.1), (2.2), (2.3), and (2.4) it is clear that the n fluxes in any mean velocity reference frame cannot all be independent. Indeed, the fluxes are related by

$$\sum_{i=1}^n \frac{w_i^R}{\rho_i} J_i^R = 0 \quad . \quad (2.5)$$

Equation (2.5) provides an alternative definition for the reference frame R and was used as such by Kirkwood and others (1960). These authors also pointed out that the fluxes with respect to *any* two reference frames may be related using the expression

$$J_i^R = J_i^S + \rho_i \bar{v}^{SR} \quad (2.6)$$

where \bar{v}^{SR} is the velocity of reference frame S with respect to reference frame R. For mean velocity reference frames we have

$$\bar{v}^{SR} = \bar{v}^{SL} - \bar{v}^{RL} = \sum_{k=1}^n (w_k^S - w_k^R) v_k^L \quad . \quad (2.7)$$

Equations (2.6) and (2.7) point out a very useful feature of mean velocity reference frames: results from various mean velocity frames may be easily interrelated. This fact will be used to advantage in defining a “standard” diffusion coefficient in section 3.

Commonly used reference frames of the mean velocity type include the following:

1. Mean molar reference frame (also called number-fixed frame)

$$w_i^N = N_i = \rho_i \bar{V} \quad \sum_{i=1}^n J_i^N = 0 \quad (2.8)$$

where N_i is the mole fraction of i and where \bar{V} is the molar volume of the phase in which the diffusion occurs.

2. Mean volume reference frame

$$w_i^V = \rho_i V_i \quad \sum_{i=1}^n V_i J_i^V = 0 \quad (2.9)$$

where V_i is the partial molar volume of i .

3. K th component reference frame

$$w_i^K = \delta_{iK} \quad J_K^K = 0 \quad (2.10)$$

where δ_{ik} is the “Kronecker delta” defined such that $\delta_{ik} = 0$ if $i \neq K$ and $\delta_{ik} = 1$ if $i = K$.

4. Mean mass (barycentric) reference frame

$$w_i^M = \tilde{N}_i = \tilde{\rho}_i \tilde{V} \quad \sum_{i=1}^n M_i J_i^M = 0 \quad (2.11)$$

where \tilde{N}_i is the mass fraction of i , $\tilde{\rho}_i$ is the mass density of i , \tilde{V} is the specific volume, and M_i is the gram-formula weight of i .

Each of these reference frames may be particularly useful for a given set of additional constraints. For example, the mean volume reference frame is most convenient if there is no volume change during the diffusion process. Also, the K th component reference frame simplifies the description of a diffusion process in which the K th component does not actively participate. Because of their general utility, much of the following discussion will emphasize mean velocity reference frames.

3. FORCES, FLUXES, AND DIFFUSION COEFFICIENTS

The presence of material transport in a system as described by the molar fluxes J_i^R clearly indicates a departure from equilibrium. On a local scale, however, the departure from equilibrium for many transport processes is not great. Therefore, it is a very good approximation to describe the changes of a system in terms of *linear* functions of the forces that tend to restore equilibrium. This linear approximation has withstood the test of countless experiments. It was formulated independently as the "laws" of Darcy, Fick, Fourier, and Ohm which govern specific transport processes. Onsager (1931a, b) unified the various linear laws using a formalism that emphasizes their interrelationships.

Isothermal, isobaric diffusion is a form of material transport linearly related to the force produced by chemical potential gradients. While chemical potential gradients are independent of the choice of reference frame, the molar fluxes J_i^R are not. Thus, the linear relations between

fluxes J_i^R and forces $\left(\frac{\partial \mu_i}{\partial x}\right)_{P,T,t}$ given by

$$J_i^R = - \sum_{j=1}^n L_{ij}^R \left(\frac{\partial \mu_j}{\partial x}\right)_{P,T,t} \quad (i = 1, 2, \dots, n) \quad (3.1)$$

will vary with the choice of reference frame. Equations (3.1) *define* the phenomenological (diffusion) coefficients, L_{ij}^R , for reference frame R . μ_i is the chemical potential per mole of i , and its derivative with respect to distance x is taken at constant pressure P , temperature T , and time t . Note that in general the flux of any component i is linearly related to the chemical potential gradients of *each* of the other components. In other words, the contribution to the diffusion flux from any applied force should be considered. It should also be noted that the degree to which each force contributes to the diffusion flux of a given component

depends directly upon the reference frame selected to describe the diffusion flux.

Equations (3.1) lead to the disturbing conclusion that for an n -component system with r reference frames of interest, there are $(r)(n)^2$ phenomenological coefficients. Fortunately, these coefficients are not all independent. Onsager (1931a, b) has shown that provided the fluxes and forces are properly chosen, the n^2 coefficients for a single reference frame are subject to the relations

$$L_{ij}^R = L_{ji}^R \quad (3.2)$$

leaving only $(n)(n+1)/2$ independent coefficients for each reference frame. Hooyman and de Groot (1955) have demonstrated that linear independence of either the fluxes or forces is a sufficient, though not necessary, condition for the Onsager symmetry relations (3.2) to hold. For mean velocity reference frames the fluxes and forces of (3.1) are not independent, being related by (2.5) and the Gibbs-Duhem equation

$$\sum_{i=1}^n N_i d\mu_i = 0 \quad (\text{constant } P, T) \quad (3.3)$$

respectively. The extra terms in (3.1) may be eliminated by using (2.5) and (3.3) and selecting J_n^R and $d\mu_n$ as the dependent variables. The result is an independent set of phenomenological equations for mean velocity frames

$$J_i^R = - \sum_{j=1}^{n-1} L_{ij}^R \left[\sum_{k=1}^{n-1} \left(\delta_{jk} + \frac{w_j^R}{w_n^R} \frac{N_k}{N_j} \right) \left(\frac{\partial \mu_k}{\partial X} \right)_{P,T,t} \right] \quad (i = 1, 2, \dots, n-1) \quad (3.4)$$

as given in de Groot and Mazur (1962, p. 242). Equations (3.4) define the phenomenological coefficients L_{ij}^R which express the linear relations between the fluxes J_i^R and a set of independent forces given by the terms enclosed in brackets. The Onsager relations (3.2) become

$$L_{ij}^R = L_{ji}^R \quad (3.5)$$

This leaves $(n-1)(n)/2$ independent coefficients for a given mean velocity frame. And since the various reference frames are related by (2.6), we are left with the task of determining a total of only $(n-1)(n)/2$ independent phenomenological coefficients.

While chemical potential gradients are theoretically meaningful as the ultimate driving forces for diffusion, they have the unfortunate quality of being difficult to measure. In crystals, they may be found only by calculations based on measurements of composition gradients combined with often-unavailable thermodynamic data. Therefore, it is common practice to describe diffusion processes in terms of "practical"

diffusion coefficients $D_{ij}^{R,C}$ which are *defined* for mean velocity frames by the relations

$$J_i^R = - \sum_{j=1}^{n-1} D_{ij}^{R,C} \left(\frac{\partial C_j}{\partial x} \right)_{P,T,t} \quad (i = 1, 2, \dots, n-1) \quad (3.6)$$

where C_i is some compositional variable. Note that the diffusion coefficients $D_{ij}^{R,C}$ depend *both* on the reference frame R used to describe the fluxes and on the particular composition variable C_i whose gradient is measured. Also, note that as in (3.4) only $(n-1)$ independent fluxes and forces are considered, with J_n^R and dC_n being selected as the dependent variables. The n fluxes are connected through equation (2.5), and the n forces are connected through relations of the type

$$\sum_{i=1}^n a_i dC_i = 0 \quad (3.7)$$

which exist for the commonly used compositional variables. The a 's are constants for a given composition. For example,

$$\sum_{i=1}^n V_i d\rho_i = 0 \quad (\text{constant } P, T) \quad (3.8)$$

where V_i is the partial molar volume of i and ρ_i is the molar density of i .

Once again with the definitions (3.6) a multiplicity of $(n-1)^2(r)(c)$ diffusion coefficients has been introduced for r reference frames and c compositional variables of interest. As before, these coefficients are not all independent: the various reference frames may be related by (2.6), and relations (perhaps unknown) obviously exist between the various compositional parameters such as mole fractions and molar densities. A maximum of $(n-1)^2$ diffusion coefficients remain. These, however, are not all independent either. Comparing equations (3.4) and (3.6) we may see that the diffusion coefficients $D_{ij}^{R,C}$ are linear functions of the phenomenological coefficients with

$$D_{il}^{R,C} = \sum_{k=1}^{n-1} \sum_{j=1}^{n-1} L_{ij}^R \left[\delta_{jk} + \frac{w_j^R}{w_n^R} \frac{N_k}{N_j} \right] \left(\frac{\partial \mu_k}{\partial C_l} \right)_{P,T,C_i \neq C_l} \quad (i, l = 1, 2, \dots, n-1). \quad (3.9)$$

Since the phenomenological coefficients L_{ij}^R are not independent, but related by the $(n-1)(n-2)/2$ equations (3.5), only $(n)(n-1)/2$ of the diffusion coefficients $D_{ij}^{R,C}$ can be independent. The specific relations among the $D_{ij}^{R,C}$ may be found for a given system by solving (3.9) for the L_{ij}^R and

using (3.5). This is only possible if the derivatives $\left(\frac{\partial \mu_k}{\partial C_i}\right)_{P,T,C_i \neq C_l}$ are known. If an equation of state is unavailable, then the relations (3.5) and (3.9) cannot be used, and $(n-1)^2$ coefficients must be determined. In any event it will not, in general, be possible to choose fluxes and forces such that $D_{ij}^{R,C} = D_{ji}^{R,C}$.

While it is clear that the diffusion coefficients for the various mean velocity reference frames and compositional variables are interconnected, we are liable to find any of the $(n-1)^2(r)(c)$ possible coefficients in use. The undesirable consequence is that diffusion data from different laboratories may not be directly comparable without performing tedious calculations. It would seem preferable to select a single reference frame R and compositional variable C_i to define a "standard" diffusion coefficient through which all data would be reported and, thus, easily compared. Following the precedent set by Hooyman and others (1953) let us use the mean volume reference frame and the molar densities ρ_i to define the standard diffusion coefficients D°_{ij} with

$$J_i^V = - \sum_{j=1}^{n-1} D^{\circ}_{ij} \left(\frac{\partial \rho_j}{\partial x} \right)_{P,T,t} \quad (i = 1, 2, \dots, n-1) \quad (3.10)$$

Equations (3.10) reduce to Fick's law at constant volume in a two-component system. For diffusion with respect to a different mean velocity reference frame R with fluxes J_i^R linearly related to fluxes J_i^V by

$$J_i^R = \sum_{j=1}^{n-1} A_{ij}^{RV} J_j^V \quad (i = 1, 2, \dots, n-1) \quad (3.11)$$

the flux equations become

$$J_i^R = - \sum_{k=1}^{n-1} \left[\sum_{j=1}^{n-1} A_{ij}^{RV} D^{\circ}_{jk} \right] \left(\frac{\partial \rho_k}{\partial x} \right)_{P,T,t} \quad (i = 1, 2, \dots, n-1) \quad (3.12)$$

If a different compositional variable C_i is used the flux equations are

$$J_i^R = - \sum_{l=1}^{n-1} \left[\sum_{k=1}^{n-1} \left(\sum_{j=1}^{n-1} A_{ij}^{RV} D^{\circ}_{jk} \right) \left(\frac{\partial \rho_k}{\partial C_l} \right)_{P,T,C_i \neq C_l} \right] \left[\frac{\partial C_l}{\partial x} \right]_{P,T,t} \quad (i = 1, 2, \dots, n-1) \quad (3.13)$$

Equations (3.13), which are identical to equations (55), p. 243 of de Groot and Mazur (1962), may be considered a generalization of Fick's law to multicomponent diffusion.

Equations (3.13) reduce to particularly simple forms for two component systems which may be described in terms of a single binary (or

interdiffusion) coefficient, since $(n-1)^2$ equals one. Let us evaluate the A_{ij}^{RV} of (3.11) for a two component system and mean velocity frame R. This may be accomplished by rewriting equation (2.4) using (2.1), (2.2), and (2.3) first for reference frame R

$$J_1^R = \rho_1 v_1^L - \rho_1 \left[w_1^R v_1^L + w_2^R v_2^L \right] \quad (3.14)$$

$$J_1^R = w_2^R \left[\rho_1 (v_1^L - v_2^L) \right] \quad (3.15)$$

and then for reference frame V

$$J_1^V = w_2^V \left[\rho_1 (v_1^L - v_2^L) \right] \quad (3.16)$$

Comparing (3.15) and (3.16) we see that

$$J_1^R = \frac{w_2^R}{w_2^V} J_1^V = \frac{w_2^R}{\rho_2 V_2} J_1^V \quad (3.17)$$

Using (3.13) and (3.17) we may give a general definition of the binary diffusion coefficient D° in terms of any mean velocity frame R as

$$J_1^R = - \frac{w_2^R}{\rho_2 V_2} D^\circ \left(\frac{\partial \rho_1}{\partial x} \right)_{P,T} \left(\frac{\partial C_1}{\partial x} \right)_{P,T,t} \quad (3.18)$$

taking component 2 as the dependent component (Hooyman and others, 1953). For the mean velocity frames presented above, (3.18) becomes (de Groot and Mazur, 1962, p. 252)

$$J_1^N = - \frac{\bar{V}}{V_2} D^\circ \left(\frac{\partial \rho_1}{\partial x} \right)_{P,T,t} = - \frac{D^\circ}{\bar{V}} \left(\frac{\partial N_1}{\partial x} \right)_{P,T,t} \quad \left(\begin{array}{c} \text{mean molar} \\ \text{frame} \end{array} \right) \quad (3.19)$$

$$J_1^V = - D^\circ \left(\frac{\partial \rho_1}{\partial x} \right)_{P,T,t} \quad \left(\begin{array}{c} \text{mean volume} \\ \text{frame} \end{array} \right) \quad (3.20)$$

$$J_1^2 = - \frac{D^\circ}{\rho_2 V_2} \left(\frac{\partial \rho_1}{\partial x} \right)_{P,T,t} = - \frac{D^\circ}{N_2 \bar{V}} \left(\frac{\partial N_1}{\partial x} \right)_{P,T,t} \quad \left(\begin{array}{c} \text{component 2} \\ \text{frame} \end{array} \right) \quad (3.21)$$

$$J_1^M = - \frac{\tilde{N}_2}{\rho_2 V_2} \left(\frac{\partial \rho_1}{\partial x} \right)_{P,T,t} = - \frac{D^\circ}{M_1 \tilde{V}} \left(\frac{\partial \tilde{N}_1}{\partial x} \right)_{P,T,t} \quad \left(\begin{array}{c} \text{mean mass} \\ \text{frame} \end{array} \right). \quad (3.22)$$

4. THE CONTINUITY EQUATION

The flux equations presented in section 3 involve gradients of chemical potentials or composition variables evaluated at any single time t . Equations (3.4) and (3.13), therefore, are "instantaneous" flux equations. They are valid to describe the process of diffusion only at a given point in space and at one particular time. The one exception is the special case of steady-state diffusion, in which the gradients of chemical potential or composition do not change with time. In general, diffusion is a non-steady-state process and must be described by a form of the continuity equation.

For diffusive mass transfer the equation of continuity is also commonly called the conservation of mass equation or the mass balance equation. It is typically given in terms of fluxes measured with respect to a laboratory reference frame. As discussed in section 2, laboratory reference frames have a number of undesirable features. In addition to those features already mentioned, laboratory frames require the use of more diffusion coefficients than mean velocity frames. Since there is, in general, no equation similar to (2.5) to interrelate laboratory frame fluxes, it will be necessary to determine n^2 diffusion coefficients $D_{ij}^{L,C}$ defined by

$$J_i^L = - \sum_{j=1}^n D_{ij}^{L,C} \left(\frac{\partial C_j}{\partial x} \right)_{P,T,t} \quad (i = 1, 2, \dots, n) \quad (4.1)$$

for any laboratory frame of interest. (The number of diffusion coefficients may be reduced to $(n)(n+1)/2$ using (3.1) and (3.2) if an equation of state is available.) It will be to our advantage, therefore, to express the continuity equation in terms of mean velocity frame fluxes.

The equation of continuity has been derived numerous times for a multitude of processes, so I will not repeat the derivation here. See Landau and Lifshitz (1959, p. 1-2) for a general derivation. In the notation of this paper the continuity equation for any component i is

$$\left(\frac{\partial \rho_i}{\partial t} \right)_{P,T,x} = - \left[\frac{\partial (\rho_i \bar{v}_i^L)}{\partial x} \right]_{P,T,t} = - \left(\frac{\partial J_i^L}{\partial x} \right)_{P,T,t} \quad (4.2)$$

Equation (4.2) is strictly applicable only to *conservative* processes in which component i is neither added to nor subtracted from the diffusive system (by reaction, for example). For constant volume diffusion, equation (4.2) has been called Fick's second law. Recalling equation (2.6), we may readily write the continuity equation for any reference frame, R, as

$$\left(\frac{\partial \rho_i}{\partial t} \right)_{P,T,x} = - \left[\frac{\partial}{\partial x} (J_i^R + \rho_i \bar{v}^{RL}) \right]_{P,T,t} \quad (4.3)$$

where \bar{v}^{RL} is the local velocity of reference frame R with respect to the laboratory frame. The value of \bar{v}^{RL} for a given mean velocity frame R may be expressed in terms of laboratory frame fluxes by using (2.5) as well as (2.6) (see Kirkwood and others, 1960). For the mean molar reference frame, N,

$$\bar{v}^{NL} = \bar{v} \sum_{i=1}^n J_i^L \quad (4.4)$$

which upon substitution into (4.3) gives

$$\left(\frac{\partial \rho_i}{\partial t} \right)_{P,T,x} = - \left(\frac{\partial J_i^N}{\partial x} \right)_{P,T,t} - N_i \sum_{k=1}^n \left(\frac{\partial J_k^L}{\partial x} \right)_{P,T,t} \quad (4.5)$$

Similarly, for the mean volume reference frame

$$\left(\frac{\partial \rho_1}{\partial t}\right)_{P,T,x} = -\left(\frac{\partial J_1^V}{\partial x}\right)_{P,T,t} - \rho_1 \left[\sum_{k=1}^n \left(\frac{\partial}{\partial x} (V_k J_k^L)\right)_{P,T,t} \right]. \quad (4.6)$$

We are now in a position to understand some of the problems of treating non-steady-state diffusion. If a laboratory frame and equation (4.2) are used, then a minimum of $(n)(n+1)/2$ diffusion coefficients must be determined. And even for a two-component system, this would be three diffusion coefficients that must be determined from two simultaneous non-linear differential equations. If a mean velocity frame is used, a minimum of only $(n)(n-1)/2$ diffusion coefficients are needed: one for a binary system, three for a ternary system. Thus, for a binary system there may be some hope, if a mean velocity frame is used. However, the continuity equation for mean velocity frames (4.3) involves the term \bar{v}^{RL} which complicates the solution.

As a consequence of these considerations, the overwhelming majority of diffusion studies has been restricted to binary systems. Generally, a mean velocity frame is chosen to limit the number of unknown diffusion coefficients to one. In addition, simplifying assumptions are made that lead to the conclusion that $\bar{v}^{RL} = 0$. In such cases the laboratory frame, L, would coincide with the mean velocity frame, R, and the continuity equation is correspondingly simplified to the form of (4.2). The most commonly used assumption is that there is no overall volume change during the diffusion process. This is equivalent to assuming that $\Delta \bar{V}_{\text{mixing}} = 0$ or that V_1 and V_2 are constant, which means that $\bar{v}^{VL} = 0$. Assuming constant volume and using (3.20), the continuity equation (4.6) for the binary case becomes

$$\left(\frac{\partial \rho_1}{\partial t}\right)_{P,T,x} = -\left(\frac{\partial J_1^V}{\partial x}\right)_{P,T,t} = \left[\frac{\partial}{\partial x} \left(D^\circ \left[\frac{\partial \rho_1}{\partial x} \right]_{P,T,t} \right) \right]_{P,T,t}. \quad (4.7)$$

Equation (4.7), which is strictly valid only for constant-volume, binary diffusion, has been solved for specific boundary conditions by Matano (1933) using the methods of Boltzmann (1894). The Boltzmann-Matano solution to (4.7), which may be evaluated using a graphical integration, is typically used by experimentalists to determine D° when D° varies with composition.

If D° can be shown to be independent of position x in the diffusion couple, (4.7) simplifies to

$$\left(\frac{\partial \rho_1}{\partial t}\right)_{P,T,x} = D^\circ \left(\frac{\partial^2 \rho_1}{\partial x^2}\right)_{P,T,t} \quad (4.8)$$

which has many solutions for a great variety of boundary conditions (see Carslaw and Jaeger, 1947; or Crank, 1956). The applicability of (4.8)

may be tested for a given set of boundary conditions by comparing the resulting composition profiles with those predicted by the appropriate analytical solution. Diffusion studies using radioactive tracers are correctly described by (4.8) due to the very small composition changes involved. Solutions to the continuity equation (4.3) for three or more components have been given in analytical form only for systems in which the diffusion coefficients D_{ij}° are independent of composition (for example, Fujita and Gosting, 1956; Kirkaldy, 1959; Oishi, 1965). Application of these solutions to ternary diffusion problems may be found in Miller (1959, 1960), Kirkaldy and Brown (1963), Carmen (1968a, 1968b), Cooper and Varshneya (1968), Varshneya and Cooper (1972a, b, and c), and Gupta and Cooper (1971).

5. $\Delta \bar{V}_{\text{mixing}}$ AND THE UNIT CELL FRAME

Unfortunately, there are many interesting two-component systems for which there is an overall volume change during a diffusion process. In these cases, (4.7) is strictly incorrect and, though often used, may be a poor approximation (Greskovich and Stubican, 1970). Correct solutions of (4.3) which allow for volume changes have been obtained by several individuals (Prager, 1953; Crank, 1956, p. 236; Balluffi, 1960; and Wagner, 1969). Each of these solutions makes use of the Boltzmann substitution and solves for D° , as defined in this paper ($D^{\circ} = D$ of Prager and Balluffi; $D^{\circ} = D^v$ of Crank (11.73); $D^{\circ} = \bar{D}$ of Wagner). Balluffi shows how his solution may be evaluated graphically. Of course, in all cases the molar volumes must be known as a function of composition. In addition, all these papers assume there is no change in the cross-sectional area of the sample normal to the diffusion direction. This assumption, while it has some basis in experiment (da Silva and Mehl, 1951; Resnick and Balluffi, 1955) for fcc metals, has been given no general justification.

An alternative approach was proposed by Hartley and Crank (1949) (reprinted in Crank, 1956, p. 219 and following). They suggested that a modified distance scale (and consequent modified concentration scale) be introduced to preserve the continuity equation in the form of (4.7), even when there is a volume change. If the mathematical form of (4.7) is maintained, then the Boltzmann-Matano approach can be used to obtain the correct solution for D° . An interesting feature of the treatment by Hartley and Crank is that the modified distance scales they proposed coincide with the set of points used to define various mean velocity reference frames. For example, their reference frame based on cross sections "fixed with respect to total mass" can be shown to be identical with the mean mass (barycentric) frame of this paper. In the barycentric case, their modified distance parameter, ξ_M , which is "measured so that equal increments of ξ_M always include equal increments of total mass" is clearly consistent with the definition (2.11) of reference points or cross sections across which there is no *net* mass flux.

The approach of Hartley and Crank is perhaps best illustrated using a modified distance scale for crystals based on the length of a unit cell

edge. For example, if there is a volume change during a diffusion process, it should be clear that the individual unit cell dimensions will vary in a manner proportional to the local volume change. Let us restrict the discussion to crystals with orthorhombic or higher symmetry. Then using the appropriate unit cell edge, say c , to define a distance parameter, ξ_N^c , ensures that equal increments of ξ_N^c involve an equal number of unit cells. It is possible, therefore, to derive a continuity equation similar to (4.7) using the distance parameter ξ_N^c and a mass balance argument.

The unit cell of a crystal is a particularly convenient frame of reference for conceptualizing the many diffusion problems for which the total number of unit cells is constant. For a unit cell reference frame to be practical, however, it must be possible to relate diffusion coefficients determined using the unit cell frame to the standard diffusion coefficients, D_{ij}° . This will always be possible if the chemical components used in the description are properly selected (Brady, 1975). Specifically, if components are chosen such that the total number of moles of these components per unit cell is constant, then equal increments of ξ_N^c will involve equal numbers of moles as well as equal numbers of unit cells. The distance parameter, ξ_N^c , therefore, would mark the distances between a set of points that may be used to define a mean molar reference frame, N . The flux of component one across a unit cross section identified with a particular ξ_N^c would then be given by J_1^N evaluated at that ξ_N^c . The flux across the ab face of a single unit cell is $(ab)(J_1^N)$, where a and b are the cell parameters normal to the diffusion direction.

Let us define the distance parameter, ξ_N^c , as follows

$$d\xi_N^c \equiv \frac{dx}{c} \quad (5.1)$$

where c is the length of the unit-cell edge in the diffusion direction. The modified concentration parameter, n_i^c , in this case defined as the number of moles of component i per unit cell, is simply the mole fraction N_i times the total number of moles per unit cell:

$$n_i^c \equiv N_i \frac{(abc)}{\bar{V}} \quad (5.2)$$

Recalling (3.19) and using (5.1) and (5.2), the flux of component one across the unit-cell face ab is given by

$$(ab)J_1^N = -\frac{(ab)}{\bar{V}} D^\circ \left(\frac{\partial N_1}{\partial x} \right)_{P,T,t} = -\frac{D^\circ}{c^2} \left(\frac{\partial n_1^c}{\partial \xi_N^c} \right)_{P,T,t} \quad (5.3)$$

Equation (5.3) is strictly true only if the total number of moles per unit cell is not a function of composition so that $\bar{V}/(abc)$ is constant. The modified continuity equation can be determined by considering the change in content of component one in the unit cell per unit time in

terms of the divergence of the flux of component one across unit-cell faces ab . The modified continuity equation is

$$\left(\frac{\partial n_1^c}{\partial t}\right)_{P,T,\xi_N^c} = -\left[\frac{\partial}{\partial \xi_N^c} \left((ab)J_1^N \right)\right]_{P,T,t} = \left[\frac{\partial}{\partial \xi_N^c} \left(\frac{D^\circ}{c^2} \left[\frac{\partial n_1^c}{\partial \xi_N^c} \right]_{P,T,t} \right)\right]_{P,T,t} \quad (5.4)$$

or using (5.2)

$$\left(\frac{\partial N_1}{\partial t}\right)_{P,T,\xi_N^c} = \left[\frac{\partial}{\partial \xi_N^c} \left(\frac{D^\circ}{c^2} \left[\frac{\partial N_1}{\partial \xi_N^c} \right]_{P,T,t} \right)\right]_{P,T,t} \quad (5.5)$$

Equation (5.5) is clearly in the same mathematical form as (4.7). It may be evaluated graphically with the usual Boltzmann-Matano procedure using a plot of N_1 versus ξ_N^c . To obtain ξ_N^c for each position $x = X$, equation (5.1) must be integrated to yield

$$\xi_N^c = \int_0^X \frac{dx}{c} \quad (5.6)$$

where $x = 0$ when $\xi_N^c = 0$ which is at the "Matano interface" defined by

$$\int_{N_1(-\infty)}^{N_1(+\infty)} \xi_N^c dN_1 = 0 \quad (5.7)$$

or alternatively by

$$\int_{-\infty}^0 [N_1(-\infty) - N_1] d\xi_N^c = \int_0^{+\infty} [N_1 - N_1(+\infty)] d\xi_N^c \quad (5.8)$$

where $N_1(+\infty)$ and $N_1(-\infty)$ correspond to the compositions far removed from the site of diffusion, as specified by the boundary conditions. Using (5.1), (5.8) becomes

$$\int_{-\infty}^0 \left[\frac{N_1(-\infty) - N_1}{c} \right] dx = \int_0^{+\infty} \left[\frac{N_1 - N_1(+\infty)}{c} \right] dx \quad (5.9)$$

If there is no change in the cross-sectional area of the sample, that is if the product (ab) is constant, then c may be replaced by \bar{V} in equations (5.1) and (5.5) to obtain the result of Cohen, Wagner, and Reynolds (1953, 1954). Thus, using the unit cell reference frame, a solution for D° may be obtained when there is a $\Delta \bar{V}_{\text{mixing}}$ by purely graphical means from the composition-distance profile and knowledge of the cell parameter c as a function of composition.

For monoclinic or triclinic crystals, the situation is more complicated. First of all, the diffusion direction should be parallel to one of the "principal" diffusion axes (Nye, 1957) so that the diffusion flux is one-dimensional. The principal diffusion directions generally will not all coincide with the crystal axes, as is the case with crystals of orthorhombic or higher symmetry, so the modified distance parameter would have to utilize a lattice translation which may not correspond to any commonly used unit cell dimension. However, since angular changes as well as volume changes may occur when the composition varies, the diffusion flux across any one crystallographic plane may not be easily determined. Therefore, the simple approach used here is not directly applicable to monoclinic or triclinic crystals if the crystallographic angles α , β , and γ change appreciably with composition.

For some common minerals, though, the variations of lattice angles accompanying compositional changes are small. Since diffusion paths are highly structure sensitive, it is probably valid to assume for these minerals that the variations in orientation of the principal diffusion directions are also small. Thus, it may be a very good approximation to treat these crystals in the manner discussed above, selecting distance parameters based on lattice translations parallel to the principal diffusion directions. The "unit cell" in this case may not correspond to any unit cell normally used. While only an approximation, this approach may yield reasonable results for some otherwise complex monoclinic or triclinic minerals.

6. INERT MARKER REFERENCE FRAME

Observations by Kirkendall (1942), Smiegelskas and Kirkendall (1947), and Hartley (1946) combined with subsequent analyses by Darken (1948) and Hartley and Crank (1949) have led to the definition of a reference frame and associated diffusion coefficients different from any yet considered in this paper. Deeply involved in the definition of this additional reference frame is the question, "What is diffusion?" or "Is all the flux measured in a given reference frame appropriately called 'diffusive flux?'". These questions were raised, and answers were clearly presented by both Darken (1948) and Hartley and Crank (1949). The conclusion reached in both papers was that a distinction should be made between a flux due to "diffusion" of an individual component relative to the others and a flux due to the "bulk flow" of all components at the same rate in the same direction. This distinction is of considerable practical importance, for Hartley's and Kirkendall's experiments demonstrated that if one component diffuses more rapidly than the other in a binary interdiffusion experiment, a bulk flow will occur. As the concept of a bulk flow generated by diffusion can be confusing, I strongly recommend the excellent discussions by Darken (1948) and Hartley and Crank (1949) to any reader who finds this concept unfamiliar.

In order to measure flux due to diffusion only, a reference frame is defined in terms of a set of points, each of which moves with the local bulk flow. Operationally, this would consist of a set of "inert" markers,

which do not participate in the diffusion, but which will move with the bulk flow. For Kirkendall, these inert markers were platinum wires in a copper-brass diffusion couple. We can define, then, inert marker diffusion coefficients, $D_{ij}^{I,C}$, in terms of the fluxes, J_i^I , given with respect to the inert marker reference frame, I , as

$$J_i^I = - \sum_{j=1}^n D_{ij}^{I,C} \left(\frac{\partial C_j}{\partial x} \right)_{P,T,t} \quad (i = 1, 2, \dots, n) \quad (6.1)$$

where C_j is some compositional parameter. As in the case of the laboratory frame (4.1), there is, in general, no relation similar to (2.5) which relates the n independent fluxes of the inert marker frame. Inert marker diffusion coefficients have been called "intrinsic" diffusion coefficients by Hartley and Crank (1949) and others. However, the title inert marker coefficient is to be preferred since the term "intrinsic" is also commonly used to describe diffusion in pure crystals in the absence of "extrinsic" effects due to impurities, grain boundaries, et cetera.

It will be useful to relate the inert marker diffusion coefficients, $D_{ij}^{I,C}$, to the standard diffusion coefficients, D_{ij}° , defined in (3.10). Recalling (2.6) we have

$$J_i^N = J_i^I + \rho_i \bar{v}^{IN} \quad (6.2)$$

Summing both sides of (6.2) over all i and using (2.8), \bar{v}^{IN} may be expressed in terms of the J_i^I . Substituting the results for \bar{v}^{IN} in (6.2) we have

$$J_i^N = J_i^I - N_i \left[\sum_{j=1}^n J_j^I \right] \quad (6.3)$$

For a two component system, then,

$$J_1^N = J_1^I - N_1 (J_1^I + J_2^I) = N_2 J_1^I - N_1 J_2^I \quad (6.4)$$

Substituting for J_1^N from (3.19) and for J_i^I from (6.1), (6.4) becomes

$$\begin{aligned} \frac{-\bar{V}}{V_2} D^\circ \left(\frac{\partial \rho_1}{\partial x} \right)_{P,T,t} &= N_2 \left[-D_{11}^{I,\rho} \left(\frac{\partial \rho_1}{\partial x} \right)_{P,T,t} - D_{12}^{I,\rho} \left(\frac{\partial \rho_2}{\partial x} \right)_{P,T,t} \right] \\ &\quad - N_1 \left[-D_{21}^{I,\rho} \left(\frac{\partial \rho_1}{\partial x} \right)_{P,T,t} - D_{22}^{I,\rho} \left(\frac{\partial \rho_2}{\partial x} \right)_{P,T,t} \right] \end{aligned} \quad (6.5)$$

Using the thermodynamic relation

$$\left(\frac{\partial \rho_2}{\partial \rho_1} \right)_{P,T} = - \frac{V_1}{V_2} \quad (6.6)$$

equation (6.5) leads to

$$\frac{D^{\circ\bar{V}}}{V_2} = N_2 \left[D_{11}^{I,\rho} - \frac{V_1}{V_2} D_{12}^{I,\rho} \right] - N_1 \left[D_{21}^{I,\rho} - \frac{V_1}{V_2} D_{22}^{I,\rho} \right] \quad (6.7)$$

If we then take the traditional approach and neglect $D_{12}^{I,\rho}$ and $D_{21}^{I,\rho}$, we obtain the relation

$$D^\circ = (\rho_2 V_2) D_{11}^{I,\rho} + (\rho_1 V_1) D_{22}^{I,\rho} \tag{6.8}$$

which was given by Hartley and Crank (1949, eq 31) for the case of constant volume, an assumption we have not made. Actually, Hartley and Crank's D^V is equivalent to D° in all respects except their conception of it. They stated that their D^V is meaningless, if there is an overall volume change. However, mathematically their D^V has meaning for all systems. Compare their equation (4) with equation (2.9) of this paper. A relation similar to (6.8) was also obtained by Darken (1948, eq 7)

$$D^\circ = N_2 D_{11}^{I,\rho} + N_1 D_{22}^{I,\rho} \tag{6.9}$$

which follows from (6.8) if $V_1 = V_2 = \bar{V}$.

Although (6.1) is consistent with the classical definition of inert marker diffusion coefficients, I prefer the following alternative definition

$$J_i^I = \sum_{j=1}^n \frac{D_{ij}^{I,N}}{\bar{V}} \left(\frac{\partial N_j}{\partial x} \right)_{P,T,t} \tag{6.10}$$

This definition leads to simpler mathematical forms for several important relationships. For example, let us relate the diffusion coefficients $D_{ij}^{I,N}$ to the standard diffusion coefficient D° for a two component system. Using (3.19) and (6.10) equation (6.4) becomes

$$\begin{aligned} -\frac{D^\circ}{\bar{V}} \left(\frac{\partial N_1}{\partial x} \right)_{P,T,t} &= N_2 \left[\frac{-D_{11}^{I,N}}{\bar{V}} + \frac{D_{12}^{I,N}}{\bar{V}} \right] \left(\frac{\partial N_1}{\partial x} \right)_{P,T,t} \\ &\quad - N_1 \left[\frac{-D_{21}^{I,N}}{\bar{V}} + \frac{D_{22}^{I,N}}{\bar{V}} \right] \left(\frac{\partial N_1}{\partial x} \right)_{P,T,t} \end{aligned} \tag{6.11}$$

from which it follows that

$$D^\circ = N_2 [D_{11}^{I,N} - D_{12}^{I,N}] + N_1 [D_{22}^{I,N} - D_{21}^{I,N}] \tag{6.12}$$

If we then define D_1^I and D_2^I as

$$\left. \begin{aligned} D_1^I &\equiv D_{11}^{I,N} - D_{12}^{I,N} \\ D_2^I &\equiv D_{22}^{I,N} - D_{21}^{I,N} \end{aligned} \right\} \tag{6.13}$$

(6.12) may be written as

$$D^\circ = N_2 D_1^I + N_1 D_2^I \tag{6.14}$$

Equation (6.14), which has the simple form of Darken's relation (6.9), is valid even if $V_1 \neq V_2$ and also if $D_{12}^{I,N}$ and $D_{21}^{I,N}$ are not negligible.

In order to obtain the values of the diffusion coefficients D_1^I and D_2^I in (6.14) a measurement of D° is necessary. This is not sufficient, however; a measurement of the velocity, $\bar{v}^{I,N}$, of the inert marker frame relative to

the mean molar frame is needed for the following relation (see (6.2) and (6.3), using also (6.10) and (6.13)):

$$\bar{v}^{IN} = -\bar{V} \left[\sum_{i=1}^n J_i^I \right] = D_1^I \left(\frac{\partial N_1}{\partial x} \right)_{P,T,t} + D_2^I \left(\frac{\partial N_2}{\partial x} \right)_{P,T,t} \quad (6.15)$$

$$\bar{v}^{IN} = \left(D_1^I - D_2^I \right) \left(\frac{\partial N_1}{\partial x} \right)_{P,T,t} . \quad (6.16)$$

Darken (1948) derived a form of (6.16) for the special case where $V_1 = V_2 = \bar{V}$ and, therefore, $\bar{v}^{NL} = \bar{v}^{VL} = 0$. Equation (6.16) may be used with (6.14) to solve for D_1^I and D_2^I at a given composition from measurements of D° (as in the last section) and \bar{v}^{IN} (as follows). To obtain \bar{v}^{IN} at a single position and time, the velocity of a marker, \bar{v}^{IL} , at that position and time (relative to the laboratory frame) must be determined by a series of measurements, at several times, of the position of the marker. The marker velocity is then compared with the velocity, \bar{v}^{NL} , of the mean molar reference frame at the same position and time.

In a binary interdiffusion experiment, the location of the points or cross sections that define the mean molar reference frame may be obtained in a fashion similar to that used to locate the "Matano interface" (5.7) or (5.9). Indeed, the Matano interface itself is a mean molar reference cross section. That this is true may be seen from (5.7) or (5.9) which require that the $x = 0$, $\xi_N^c = 0$ cross section be one such that the cumulative flux of atoms across the cross section in one direction equals the cumulative flux of atoms across the cross section in the other direction. Other cross sections across which the cumulative atom fluxes in both directions balance are given by

$$\int_{N_1(-\infty)}^{N_1(+\infty)} \xi_N^c dN_1 = k \quad (6.17)$$

or

$$\int_{-\infty}^0 \left[\frac{N_1(-\infty) - N_1}{c} \right] dx = \int_0^{+\infty} \left[\frac{N_1 - N_1(+\infty)}{c} \right] dx + k \quad (6.18)$$

where k is a constant, different for each cross section. Equations (6.17) and (6.18) define an $x = 0$, $\xi_N^c = 0$ plane which is a mean molar reference cross section (see fig. 1). Thus, to evaluate \bar{v}^{IN} , one needs to determine the k for the mean molar reference plane which coincides in position with the inert marker used to determine \bar{v}^{IL} at the appropriate time. One then determines \bar{v}^{NL} for the mean molar plane identified with that k by a series of calculations at several times of the position of that plane. Alternatively, one could use (5.6) and (5.9) to locate the plane associated with

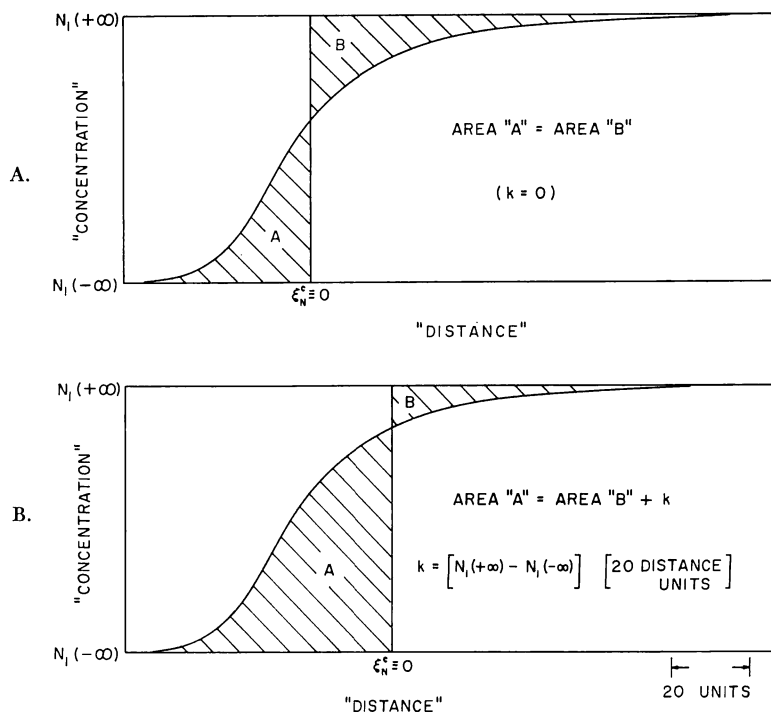


Fig. 1. "Concentration" versus "distance" profile for a binary interdiffusion experiment with the "Matano interface" of equation (5.11) shown in (A) and a mean molar plane k of equation (6.18) shown in (B) with $k = [N_1(+\infty) - N_1(-\infty)] \times [20 \text{ distance units}]$.

a given ξ_N^c at various times, which would involve more effort than using (6.18).

7. DARKEN'S EQUATION AND TRACER DIFFUSION COEFFICIENTS

There is reason to believe that the inert marker frame coefficients presented above are in some ways more "fundamental" than the mean velocity frame diffusion coefficients; hence, the often used name "intrinsic" diffusion coefficients (suggested by Hartley and Crank, 1949). The argument is based on the assumption that the principal effect of the motion of one component upon the motion of another component is the flux due to bulk flow. Therefore, if the effect of a bulk flow is eliminated by using an inert marker frame, then the flux of a component might be expected to depend only upon gradients of its own chemical potential. In other words, an assumption is made that the off-diagonal terms in the phenomenological equations (3.1) are necessary *only* to account for flux due to bulk flow.

The validity and consequences of the assumption of negligible off-diagonal ($i \neq j$) phenomenological coefficients, L_{ij}^I , for the inert marker frame have been discussed by many individuals (Bardeen and Herring,

1951; LeClaire, 1953; Manning, 1961, 1968; Shewmon, 1963; Howard and Lidiard, 1964; Ziebold and Cooper, 1965; Carmen, 1968a, b). The consensus is that the assumption is not correct but may be a good approximation for many systems. Carmen (1968a, b) argues that it is a poor approximation for "complex Darken systems" where a single component may be present in more than one diffusing species. Manning (1968) uses an atomistic approach to demonstrate that the assumption cannot be strictly correct for diffusion in solids by a vacancy mechanism. Nevertheless, the estimated errors that might be caused by neglecting the off-diagonal terms in the inert marker frame are within the range of uncertainty of measurement on many solids or other "simple Darken systems". With this in mind, it is worthwhile to explore a very useful consequence of the assumption.

Two isotopes of the same element are chemically quite similar. The electron shells surrounding each of the slightly different nuclei of the two isotopes behave identically in many interactive situations. Therefore, it is not unreasonable to assume that the motion of either isotope in response to an identical chemical force (chemical potential gradient) would be the same (in the absence of gravitational effects). This assumption was expressed by Darken (1948) as an equality of mobilities, B_i^I , which give the velocity of a component in response to a unit force. In terms of equation (3.1), B_i^I is defined as follows (neglecting the off-diagonal coefficients):

$$J_i^I = -L_i^I \left(\frac{\partial \mu_i}{\partial x} \right)_{P,T,t} = -B_i^I \left(\frac{N_i}{V} \right) \left(\frac{\partial \mu_i}{\partial x} \right)_{P,T,t} \quad (7.1)$$

and Darken's equality would be

$$(B_i^I)^* = B_i^I \quad (7.2)$$

where the * refers to a radioactive isotope of component i .

The next step is to compare the diffusion coefficient determined in a tracer "self-diffusion" experiment (mixing of two isotopes of the same element) with the inert marker coefficients (6.13). To do this we must relate the mobilities, B_i^I , to the inert marker diffusion coefficients. Writing (6.10) for a two component system and using (6.13) we obtain upon comparison with (7.1)

$$J_i^I = -B_i^I \left(\frac{N_i}{V} \right) \left(\frac{\partial \mu_i}{\partial x} \right)_{P,T,t} = -\frac{D_i^I}{V} \left(\frac{\partial N_i}{\partial x} \right)_{P,T,t} \quad (7.3)$$

and

$$D_i^I = B_i^I N_i \left(\frac{\partial \mu_i}{\partial N_i} \right)_{P,T} = B_i^I \left(\frac{\partial \mu_i}{\partial \ln N_i} \right)_{P,T} \quad (7.4)$$

The molar chemical potential, μ_i , is related to the mole fraction, N_i , by

$$\mu_i = \mu_i^\circ + RT \ln N_i \gamma_i \quad (7.5)$$

where γ_i is the activity coefficient necessary to correct for non-ideality.

Using (7.5) to evaluate (7.4) we have:

$$D_1^I = B_1^I RT \left[\frac{\partial \ln(N_1 \gamma_1)}{\partial \ln N_1} \right]_{P,T} = B_1^I RT \left[1 + \left(\frac{\partial \ln \gamma_1}{\partial \ln N_1} \right)_{P,T} \right]. \quad (7.6)$$

In a tracer "self-diffusion" measurement, there is, ideally, only mixing of isotopes of the same element. For isotopic mixing, which is chemically ideal, (7.6) becomes:

$$(D_1^I)^* = (B_1^I)^* RT \quad . \quad (7.7)$$

Since the mole fraction of the minor isotope in a tracer self-diffusion experiment is very small, the diffusion coefficient measured, D° , will be equal to the intrinsic diffusion coefficient of the tracer, $(D_1^I)^*$, (see 6.14). This is strictly true only in the binary isotopic end member systems. For a detailed phenomenological discussion, see Howard and Lidiard (1964, p. 207 and following). Using (7.2), (7.6), and (7.7), then, we obtain the desired relation

$$D_1^I = (D_1^I)^* \left[1 + \left(\frac{\partial \ln \gamma_1}{\partial \ln N_1} \right)_{P,T} \right] \quad . \quad (7.8)$$

Using the identity

$$\left[\frac{\partial \ln \gamma_1}{\partial \ln N_1} \right]_{P,T} = \left[\frac{\partial \ln \gamma_2}{\partial \ln N_2} \right]_{P,T} \quad (7.9)$$

which follows from (7.5) and the Gibbs-Duhem equation (3.3), we may substitute (7.8) into (6.14) to obtain a version of Darken's equation (1948, eq 18)

$$D^\circ = \left[N_2 (D_1^I)^* + N_1 (D_2^I)^* \right] \left[1 + \left(\frac{\partial \ln \gamma_1}{\partial \ln N_1} \right)_{P,T} \right] \quad . \quad (7.10)$$

The practical importance of (7.10) is great indeed. To the extent that (7.10) is correct, measurements of diffusion coefficients using radioactive tracers may be used to predict binary interdiffusion behavior. This is particularly important for those interested in determining diffusion coefficients which are very small, for example, in minerals at metamorphic temperatures. This is a result of the fact that small concentrations of a radioactive isotope may be detected with considerably more precision than small concentrations of non-radioactive species.

8. IONIC CRYSTALS

Crystals that have an appreciable ionic character such as halides, oxides, and silicates present some additional constraints which have not been considered above. Specifically, the strict stoichiometry required to maintain electrical neutrality leads to a coupling of fluxes for an interdiffusion experiment in an ionic crystal. Nevertheless, nearly all the results given above are valid for ionic crystals if the components used in the

description are *actual* components of the crystal considered. Actual components of a crystal may be both added to and subtracted from a crystal without destroying the homogeneity of that crystal (Gibbs, 1928, p. 64; Thompson, 1959; Brady, 1975). In the absence of external electric fields, any actual component of a given crystal must be electrically neutral. Therefore, the constraints of stoichiometry or electrical neutrality are automatically satisfied in any description, if actual components are used. The results of section 7, however, are not correct for ionic crystals. In particular, Darken's equation (7.10) is subject to modifications, which we shall now consider.

In ionic crystals either the positive ions move or the negative ions move, rarely both (Jost, 1952). Therefore, in the following discussion we shall consider the motion of cations in a network of stationary anions; results are equally applicable to the opposite case of mobile anions. If the anions do not diffuse, then they will behave as inert markers. So for most ionic crystals the inert marker reference frame will coincide with the unit cell reference frame and also with the mean molar frame (for a judicious choice of components). Therefore, the two inert marker diffusion coefficients (6.13) for a binary system must be identical (see 6.16). This means that there will be no "Kirkendall effect" for interdiffusion in ionic crystals and that the Matano (1933) interface will always coincide with the initial crystal-crystal interface, even if there is a $\Delta\bar{V}_{\text{mixing}}$.

In section 7 a relationship (7.10) between tracer self-diffusion coefficients and the standard binary diffusion coefficient was obtained by relating inert marker diffusion coefficients to self-diffusion coefficients. The same approach cannot be valid for ionic crystals, since the equality of the two inert marker coefficients combined with equation (7.8) would imply that the self-diffusion coefficients for the two components of a binary crystal must be equal. Experimentally, this is not the case (Askill, 1970), so equation (7.8) must not be valid for ionic crystals. A scrutiny of the steps followed in obtaining (7.8) will reveal that it is equation (7.1) that is in error for ionic crystals. The reason (7.1) is incorrect is that a force has been neglected, the force that prevents any deviations from stoichiometry. Since the mobility, B_i^I , gives the velocity of diffusion in response to a unit force, (7.1) cannot be correct if all the forces are not considered.

It is not unreasonable to assume that the force that maintains stoichiometry in ionic crystals is the large electrical potential gradient that would develop if any deviations from stoichiometry did occur. The response of a diffusing species to an electrical potential gradient is proportional to both its charge, q_i , and its mobility, B_i^I , so that the flux of

species i in response to an applied field $\left(\frac{\partial\phi}{\partial\mathbf{x}}\right)_{\text{P,T,t}}$ would be

$$J_i^I = -B_i^I \left(\frac{N_i}{\bar{V}}\right) q_i \left(\frac{\partial\phi}{\partial\mathbf{x}}\right)_{\text{P,T,t}} \quad (8.1)$$

(Jost, 1952). The flux of species i in response to both an electrical potential gradient and a chemical potential gradient is then

$$J_i^T = -B_i^T \left(\frac{N_i}{\bar{V}} \right) \left[\left(\frac{\partial \mu_i}{\partial \mathbf{x}} \right)_{P,T,t} + q_i \left(\frac{\partial \phi}{\partial \mathbf{x}} \right)_{P,T,t} \right] . \quad (8.2)$$

Assuming that (8.2) includes all the appropriate forces we might proceed as in section 7 to find a relationship similar to (7.10). Unfortunately, there is one further stumbling block. The chemical potential gradient indicated in (8.2) must be written for a charged species, since it is only for the motion of a charged species that (8.2) is needed to replace (7.1). However, the chemical potential of a charged species in a stoichiometric ionic crystal is an undefined quantity. This dilemma may be resolved by considering explicitly the possibility of vacancies and non-stoichiometry (see Howard and Lidiard, 1964) or by making a simplifying assumption that will lead to a result that may be tested experimentally. We will take the latter approach here, manipulating the chemical potentials of charged species as if they were meaningful and then expressing the result in terms of measurable quantities.

Let us begin by considering a general binary ionic crystal composed of various combinations of two cations, A^{+a} and B^{+b} , and a single anion or negatively charged component Z^{-z} . We shall explicitly include the charges $+a$, $+b$, and $-z$ to allow for the possibility of the cations having different charges. This binary ionic crystal will have actual components $A_z Z_a$ and $B_z Z_b$ where the subscripts indicate the number of moles of the cations and anions in one mole of the component. An alkali feldspar would be an example of a binary "ionic" crystals with $A^{+a} = K^{+1}$, $B^{+b} = Na^{+1}$, $Z^{-z} = (AlSi_3O_8)^{-1}$, and actual components $KAlSi_3O_8$ and $NaAlSi_3O_8$. Wustite would be another example (different in the respect that $+a \neq +b$) with $A^{+a} = Fe^{+2}$, $B^{+b} = Fe^{+3}$, $Z^{-z} = O^{-2}$, and actual components Fe_2O_2 and Fe_2O_3 .

If the crystal is in local homogeneous equilibrium, the following relations must be satisfied (Prigogine and Defay, 1954, p. 69)

$$\mu_{A_z Z_a} = z\mu_{A^{+a}} + a\mu_{Z^{-z}} \quad (8.3)$$

$$\mu_{B_z Z_b} = z\mu_{B^{+b}} + b\mu_{Z^{-z}} . \quad (8.4)$$

We have also from (3.3)

$$N_{A_z Z_a} d\mu_{A_z Z_a} + N_{B_z Z_b} d\mu_{B_z Z_b} = 0 . \quad (8.5)$$

If we assume that the chemical potential of Z^{-z} is not a function of composition, then (8.3), (8.4), and (8.5) lead to

$$\left(\frac{\partial \mu_{A^{+a}}}{\partial \mathbf{x}} \right)_{P,T,t} = \frac{1}{z} \left(\frac{\partial \mu_{A_z Z_a}}{\partial \mathbf{x}} \right)_{P,T,t} = - \left[\frac{N_{B_z Z_b}}{N_{A_z Z_a}} \right] \left(\frac{\partial \mu_{B^{+b}}}{\partial \mathbf{x}} \right)_{P,T,t} . \quad (8.6)$$

The validity of the assumption leading to (8.6) is discussed by Cooper and Heasley (1966). See also Wagner (1930) and Jost (1952, p. 146).

Let us simplify the notation slightly by letting $AZ = A_z Z_a$, $BZ = B_z Z_b$, $A = A^{+a}$, and $B = B^{+b}$. Then using (8.6), (8.2) may be written for the fluxes of A and B , respectively

$$J_A^I = -B_A^I \left(\frac{zN_{AZ}}{\bar{V}} \right) \left[\frac{1}{z} \left(\frac{\partial \mu_{AZ}}{\partial \mathbf{x}} \right)_{P,T,t} + a \left(\frac{\partial \phi}{\partial \mathbf{x}} \right)_{P,T,t} \right] \quad (8.7)$$

$$J_B^I = +B_B^I \left(\frac{zN_{BZ}}{\bar{V}} \right) \left[\frac{1}{z} \left(\frac{N_{AZ}}{N_{BZ}} \right) \left(\frac{\partial \mu_{AZ}}{\partial \mathbf{x}} \right)_{P,T,t} - b \left(\frac{\partial \phi}{\partial \mathbf{x}} \right)_{P,T,t} \right] \quad (8.8)$$

where we have used the fact that the density of A is z times the density of AZ . Due to the constraint of electrical neutrality, the fluxes of A and B with respect to the unit cell frame (= inert marker frame) must satisfy the relation

$$aJ_A^I + bJ_B^I = 0 \quad . \quad (8.9)$$

Using (8.9), (8.7) and (8.8) may be solved for $\left(\frac{\partial \phi}{\partial \mathbf{x}} \right)_{P,T,t}$ yielding

$$\left(\frac{\partial \phi}{\partial \mathbf{x}} \right)_{P,T,t} = \left(\frac{N_{AZ}}{z} \right) \frac{(bB_B^I - aB_A^I)}{(a^2N_{AZ} B_A^I + b^2N_{BZ} B_B^I)} \left(\frac{\partial \mu_{AZ}}{\partial \mathbf{x}} \right)_{P,T,t} \quad . \quad (8.10)$$

Substituting (8.10) into (8.7), it follows that

$$J_A^I = - \left(\frac{N_{AZ}}{\bar{V}} \right) \frac{(B_A^I B_B^I) (b) (aN_{AZ} + bN_{BZ})}{[a^2N_{AZ} B_A^I + b^2N_{BZ} B_B^I]} \left(\frac{\partial \mu_{AZ}}{\partial \mathbf{x}} \right)_{P,T,t} \quad . \quad (8.11)$$

In order to express the final results completely in terms of actual components, note that stoichiometry requires

$$J_A^I = zJ_{AZ}^I \quad (8.12)$$

and that (8.3) requires (since $v_A^I = v_{AZ}^I$)

$$B_A^I = zB_{AZ}^I \quad . \quad (8.13)$$

Combining (8.11), (8.12), and (8.13) then

$$J_{AZ}^I = - \left(\frac{N_{AZ}}{\bar{V}} \right) \frac{(B_{AZ}^I B_{BZ}^I) (b) (aN_{AZ} + bN_{BZ})}{[a^2N_{AZ} B_{AZ}^I + b^2N_{BZ} B_{BZ}^I]} \left(\frac{\partial \mu_{AZ}}{\partial \mathbf{x}} \right)_{P,T,t} \quad (8.14)$$

or using (7.2), (7.5), and (7.7) (which are still valid even though (7.1) is not)

$$J_{AZ}^I = \frac{-1}{\bar{V}} \frac{(D_{AZ}^I)^* (D_{BZ}^I)^* (b) (aN_{AZ} + bN_{BZ})}{[a^2N_{AZ} (D_{AZ}^I)^* + b^2N_{BZ} (D_{BZ}^I)^*]} \left[1 + \left(\frac{\partial \ln \gamma_{AZ}}{\partial \ln N_{AZ}} \right)_{P,T} \right] \left(\frac{\partial N_{AZ}}{\partial \mathbf{x}} \right)_{P,T,t} \quad . \quad (8.15)$$

Finally we must note that the mean molar reference frame for components $A_z Z_a$ and $B_z Z_b$ does *not* coincide with the unit cell frame (= inert marker frame), although the mean molar frame for components

$A_{bz} Z_{ab}$ and $B_{az} Z_{ab}$ does (see sec. 5). Using (3.19) written for these latter components and performing a simple component transformation (Brady, 1975), we obtain

$$J_{AZ}^I = \frac{-b}{(aN_{AZ} + bN_{BZ})} \frac{D^\circ}{\bar{v}} \left(\frac{\partial N_{AZ}}{\partial x} \right)_{P,T,t} \quad (8.16)$$

On comparing (8.15) and (8.16) it follows that

$$D^\circ = \frac{(D_{AZ}^I)^* (D_{BZ}^I)^* (aN_{AZ} + bN_{BZ})^2}{[a^2 N_{AZ} (D_{AZ}^I)^* + b^2 N_{BZ} (D_{BZ}^I)^*]} \left[1 + \left(\frac{\partial \ln \gamma_{AZ}}{\partial \ln N_{AZ}} \right)_{P,T} \right] \quad (8.17)$$

which is the relation we have been looking for. If $a = b$ then (8.17) reduces to the simple form

$$D^\circ = \frac{(D_{AZ}^I)^* (D_{BZ}^I)^*}{[N_{AZ} (D_{AZ}^I)^* + N_{BZ} (D_{BZ}^I)^*]} \left[1 + \left(\frac{\partial \ln \gamma_{AZ}}{\partial \ln N_{AZ}} \right)_{P,T} \right] \quad (8.18)$$

as given in Manning (1968, p. 21).

Equations (8.17) and (8.18) have the potential to perform the same important function for ionic crystals that Darken's equation (7.10) performs for metallic crystals: relating relatively easy to measure self-diffusion coefficients to relatively hard to measure interdiffusion coefficients. Equation (8.17) is only an approximation, though, subject to the validity of (8.6). Unfortunately, I know of no experimental verification of (8.17), so it should be used with caution. Equation (7.10), on the other hand, is clearly incorrect for ionic crystals, although it is commonly used for ionic crystals in the literature (for example, Buening and Buseck, 1973, p. 6856; Wei and Wuensch, 1973, p. 564). Cooper and Heasley (1966) give a relation (their eq 14) similar to equation (8.15) but not identical with it. I believe their equation (14) to be incorrect, and Cooper agrees (personal commun., 1974).

Unfortunately, not all binary ionic crystals are suited to the above analysis. Consider, for example, the binary system of the plagioclase feldspars ($\text{NaAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$). Interdiffusion in this system involves the exchange of Na and Si for Ca and Al. While we might measure the tracer diffusion coefficients of Ca or Al, there is no way to ensure that doped Ca and Al remain coupled in a tracer experiment in anorthite as they must in an interdiffusion experiment between anorthite and albite. One simplification, which might be useful in practice, would be to assume that the motion of the coupled pair CaAl is limited by the motion of Al, measure the diffusion of an Al isotope, and proceed as in (8.17).

9. CONCLUDING REMARKS

Several points made in the preceding paragraphs deserve reiteration. (1) Fluxes and diffusion coefficients are meaningless quantities unless referred to a specific reference frame. (2) Certain reference frames are preferred for common usage due to the ease with which they may be inter-related; mean velocity frames are particularly convenient. (3) All diffusion data should be reported in terms of "standard" diffusion coefficients

based on the mean volume reference frame. (4) Volume changes may be significant in many diffusion processes and can be handled for single crystals using a unit cell reference frame. (5) Self-diffusion data may be used to predict interdiffusion behavior; the approximation for ionic crystals is different than for metallic crystals.

The discussion above has emphasized diffusion in single crystals, but many of the results are not so restricted. Indeed, selecting a reference frame can be particularly important for geologists considering diffusion in natural polycrystalline materials. For example, metasomatic zones generally lack complete information on the initial distribution of material so that a laboratory frame is unavailable. However, assumptions about the starting configuration and diffusion process may still be evaluated using some of the other reference frames considered in this paper (for example, Thompson, 1975).

ACKNOWLEDGMENTS

Special thanks belong to R. James Kirkpatrick, John M. Ferry, James F. Hays, Alan B. Thompson, and Steven M. Richardson for many helpful discussions on diffusion topics and comments on this paper. Early drafts of the paper were also considerably improved by the suggestions of George W. Fisher. This work is published under the auspices of the Committee on Experimental Geology and Geophysics at Harvard University.

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