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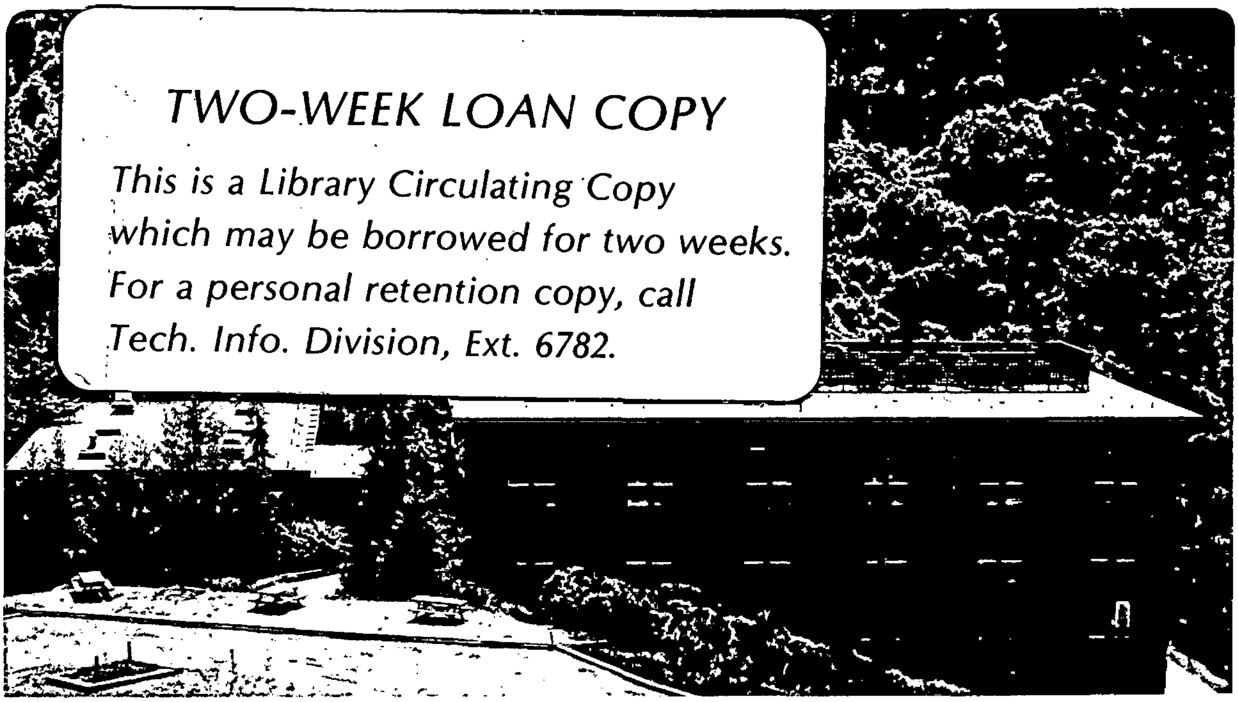

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MULTICOMPONENT DIFFUSION

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SYNOPSIS

The understanding of solid state diffusion is fundamental to that of many high temperature metallurgical phenomena. The mechanistic approach to diffusion theory is valuable as a means of interpreting diffusion data in terms of atomic structure. However, its complexity limits the scope of the mechanistic approach to very simple systems. Practically important systems, meanwhile are rarely simple and demand a theoretical framework which encompasses such multicomponent phenomena as "Uphill Diffusion". This situation demands the development of a comprehensive phenomenological theory of diffusion. However, it is important to be aware of the pitfalls of applying a phenomenological approach to such an inhomogeneous system as a solid metal.

The theme of this review is the development of ideas of solid state diffusion from Fick's Laws onwards, with particular emphasis on the area of multicomponent substitutional alloys. Recent advances in the analysis of multicomponent diffusion profiles, which render the determination of diffusion coefficients less tedious, are highlighted.

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1. INTRODUCTION

Diffusion is the process whereby the atomic or molecular particles of a system redistribute themselves within that system and, therefore, the understanding of diffusion is fundamental to that of almost all the changes of structure or chemical composition which can occur in the solid state. Such changes are the collective result of very many atomic movements, each of which is subjected to a considerable energy barrier. Thus, solid state transformations (excluding those which are diffusionless) are generally slow, although the rate increases sharply with increasing temperature. Since diffusion provides such a kinetic restaint to the attainment of thermodynamic equilibrium in solids, any study of high temperature metallurgical phenomena such as annealing, recrystallization, homogenization, kinetics of precipitation, high temperature oxidation, corrosion, creep, etc. must be based on an understanding of diffusion.

Because of the way in which ideas about diffusion developed, the correct mathematical relationships were obtained for the description of diffusion in binary systems, but they were deduced on the basis of ill-conceived theories concerning the nature of diffusion. It was not until systems of more than two components were studied that the flaws in the early ideas on diffusion became apparent. Unfortunately, most text-books dealing with diffusion introduce the subject with a discussion of Fick's Laws [1], retaining the concept that the driving force for diffusion of species is the concentration gradient of that species. By this approach, a substantial intellectual leap is required to understand diffusion in systems of more than two components. This is, perhaps, one of the reasons why studies of ternary diffusion, taking full account of the interactions between the various elements present, are few and far between. Another possible explanation lies in the general unproductivity of ternary diffusion studies in terms of the amount of experimentation required to produce a given amount of diffusion data.

It is important, however, that diffusion be studied in ternary systems, because there are two features of multicomponent diffusion which cannot be simulated in a system of less than three components. The first of these is so called "Uphill Diffusion", in which the atoms of a given species diffuse up the concentration gradient of that species. This occurs when the gradients of concentration and chemical potential are opposite in sign and it illustrates the fact that the driving force for diffusion is the latter rather than the former.

The second multicomponent effect which cannot be simulated in a binary system is the possibility of having a composition gradient through a two-phase region. This arises because the Phase Rule allows only two degrees of freedom if two phases are to exist together in equilibrium in a two component system. Thus if pressure and temperature are fixed then the compositions of the two phases in equilibrium are fixed and so it is not possible to have a composition gradient through such a region. This rules out the possibilities of internal precipitates and unstable planar interfaces in binary systems since phase boundaries in the latter must be planar and perpendicular to the composition gradient.

In addition to the above, ternary diffusion studies are of great value as a means of investigating the thermodynamic interactions between the components of a system. In particular, the effect which one component has on the Gibb's Free Energy of another is reflected directly in the sign and magnitude of the respective cross diffusion coefficient.

2. APPROACH TO DIFFUSION THEORY

There are two distinct ways in which diffusion may be analysed, each being useful under different circumstances. These are, respectively, the mechanistic and the phenomenological approaches. Of these, the most active area of study is in diffusion mechanisms because it is thus possible to ascribe some fundamental meaning to the diffusion coefficients. Hence, diffusion study can contribute much valuable information to the atomic models of solids. However, this approach is very limited in scope in that it can only cope with very simple systems. In order to deal with the complex systems met in practice, the phenomenological theory must be relied upon. However, caution must be exercised when applying a phenomenologically based diffusion theory to metals in the solid state, since the latter are rarely homogeneous structures in perfect thermodynamic equilibrium, but usually contain grain boundaries and other crystal defects. Under certain circumstances, however, the diffusion process is dominated by so called volume diffusion (i.e. through the crystal lattice rather than along grain boundaries, dislocations etc.) and it is in this regime that a phenomenological theory is valid.

In order to be aware of the extent of these limitations on the application of the phenomenological approach to diffusion, it is necessary to give some prior consideration to the nature of diffusion at the atomic level. Such a consideration will also give some insight into the shortcomings of the mechanistic approach to diffusion theory.

3. ATOMISTICS OF DIFFUSION

The atoms in a solid metal occupy specific sites in a crystal lattice structure, and a considerable energy barrier must be overcome if an atom is to move out of its site. However, at all temperatures above absolute zero, the atoms of the solid possess thermal energy which causes them to vibrate about their equilibrium positions.

From the model of a perfect gas it is possible to derive the so called Maxwell-Boltzmann distribution of energies which gives rise to the prediction that the probability (P) that an atom possesses an energy greater than or equal to a given energy (E) is given by:

$$P \propto \exp\left(\frac{-E}{kT}\right) \tag{1}$$

where,

T = Temperature °K

k = Boltzmann's Constant

$= 1.380 \times 10^{-23}$ joules deg^{-1} [2]

This same function has been found to predict quite accurately the vibrational energy distribution of the atoms in a crystalline solid [3]. Thus there is a finite probability of a given atom acquiring the energy required to overcome the barrier constraining it to a particular location in the lattice.

Having established that the atoms in a crystal can move, it is now necessary to consider the various mechanisms by which atomic motion may occur [4].

3.1 Diffusion Mechanisms

The various different mechanisms of diffusion can be grouped into two categories, that is those in which there may be more atoms per unit cell than lattice sites and, secondly, those in which atoms are constrained to move only from one lattice site to another. The first category includes the Interstitial Mechanism, the Interstitialey Mechanism, the Mechanism of Gibson et al. [5] and the Crowdion Mechanism. (Reference [4] gives full details of each of these.) For substitutional alloys of close packed metals, however, interstitial type defects produce very large lattice distortions and are consequently rare except in irradiated or cold-worked specimens. Thus, the mechanisms listed above are relatively unimportant for these materials.

Of the second category of diffusion mechanisms mentioned above (i.e in which atoms are confined to lattice sites), the earliest hypothesis was the Direct Exchange Mechanism whereby two nearest neighbour atoms simply exchange places. However, calculations later showed [6,7] that the large lattice distortions produced by this mechanism made it energetically unfavourable compared with the Vacancy Mechanism. It can be shown [3] that at any given temperature above absolute zero there is a finite equilibrium concentration of vacancies which exist in a crystal lattice given by:

$$n/N = e^{S_F/k} \, e^{-E_F/kT} \qquad (2)$$

where,

n = Number of Vacancies

N = Number of Lattice Sites

S_F = Vacancy Formation Entropy
E_F = Vacancy Formation Energy
k = Boltzmann's Constant
T = Temperature °K

This arises because the presence of vacancies in a crystal lattice contributes both to the internal energy and to the entropy of the system. Thus the opportunity exists for a system to reduce its free energy by the production of vacancies. A close packed atom can move into a vacancy with relatively little distortion and so the vacancy diffusion mechanism is favoured energetically.

In 1950, Zener [8] postulated the Ring Mechanism for diffusion as a more generalized version of the Direct Exchange Mechanism. The suggestion was that three or four atoms could move simultaneously in a ring, but calculations showed that this was still less energetically favourable than the Vacancy Mechanism for close packed metals and, indeed, there is considerable experimental evidence against the Ring Mechanism. Smigelskas and Kirkendall [9] conducted an experiment with inert markers at the interface of a diffusion couple between copper and brass. The movement of the markers in the direction of the brass side of the couple cannot be explained entirely by the change in volume on mixing. This result has been confirmed in several other systems by Da Silva and Mehl [10] and suggests that the sum of the diffusion fluxes is not zero. This observation can be explained if diffusion occurs by a vacancy mechanism, but not if either the ring or direct exchange mechanism operates.

Hence, the ring mechanism is no longer considered as a possibility in close packed alloys. However, it has been suggested that it may occur to some extent in b.c.c. metals to explain some of the anomalous diffusion coefficients obtained for such systems. The open nature of the b.c.c. lattice makes this a reasonable suggestion.

3.2 Statistical Treatment of Diffusion

In order to relate the observed macroscopic behavior of a system undergoing diffusion to the assumed mechanism, statistical mechanics is used. Consider the motion of a single atom by the vacancy mechanism through a homogeneous matrix:

Jump Frequency

This depends on the number of nearest neighbour sites which are vacant and on the time required by the atom concerned to jump into an adjacent vacant site. The second of these terms contributing to the jump frequency is very difficult to define rigorously. Rice [11] has attempted to describe the problem in terms of the vibrational modes of the atoms by assuming that the movement of a particular atom is just the sum of all the displacements caused by the random acoustic waves passing through the lattice.

In a different approach, statistical mechanics is used to determine the concentration of "activated complexes" in a system, i.e. atoms midway between two equilibrium sites. This procedure [4] gives the following expression for the average frequency (W) with which an atom jumps into an adjacent vacant site:-

$$\underline{\underline{W = v.\ \exp\ (-\Delta G/RT)}} \qquad (3)$$

where,

$$v = \frac{\text{Average velocity of atoms passing through activated complex state}}{\text{Width of barrier to motion of the atom}}$$

ΔG = Free energy of activation, for the movement of an atom to the activated complex state.

This, W is subdivided into a frequency factor (v) and a term which measures the probability of an atom having sufficient energy to overcome the barrier constraining it to its lattice site.

An atom achieves the conditions required of it to make a jump by a completely random process, so the time taken by the atom to jump is variable. However, the overall diffusion process involves such a large number of jumps that it is reasonable to consider the jump frequency as a constant, equal to the average rate of jumping.

Jump Distance

Since the atoms of a crystalline metal are constrained to jump from one lattice site to another, the jump distance is defined by the particular crystallography concerned.

Jump Direction

In order for any significant redistribution of atomic species to take place in a system by diffusion, each atom must move a considerable distance and therefore make many jumps. Thus the direction in which a given atom jumps is of some importance. As will be described later, successive atomic jumps are not entirely independent of one another, but this effect is of minor importance when dealing with pure metals.

The jump direction of diffusing atoms is also influenced by the presence of potential gradients in a system which make the activation energy for jumps in certain directions lower than in others. However, in the absence of such complications, it may be assumed that each atomic jump is entirely random in direction. Thus, it is possible to determine the probability of finding any given atom at a particular location after a particular number of jumps.

Suppose an atom makes n jumps of distance a. The final position of the atom can be described in terms of the vector $\underline{r}$, defined from the origin. The probability of the atom being found in the volume element dV (= dx·dy·dz) formed by the increment $d\underline{r}$ of $\underline{r}$ is given by [2,12]:-

$$P(\underline{r})\cdot dV = \left[\frac{b}{\pi}\right]^{3/2} \cdot \exp\left(-b\cdot|\underline{r}|^2\right)\cdot dV \qquad (4)$$

where

$$b = \frac{3}{2na^2}$$

The probability of finding the atom at some distance r from the origin is obtained by replacing dV by the volume of an elemental sphere of inner radius r and outer radius r + dr (i.e. $4\pi r^2 dr$).

$$P(r)\cdot dr = 4\pi\, r^2 \left[\frac{b}{\pi}\right]^{3/2} \cdot \exp\left(-br^2\right)\cdot dr \qquad (5)$$

From equation (5) can be found the root mean square distance that an atom will travel after n random jumps of length a:-

$$\sqrt{r^2} = a\sqrt{n} \tag{6}$$

3.3 Mechanistic Derivation of Diffusion Equation

Diffusion in metals can be investigated using radioactive tracers. Into a block of a pure metal is diffused a radioactive isotope of the same element. After a suitable annealing time, the distribution of tracer through the block is determined by taking thin slices off the block and then measuring the intensity of radiation from each slice.

A system like this is very easy to treat theoretically because, although the radioactive isotope can be readily identified in the system, its chemical behaviour is identical to that of the host stable isotope and, furthermore, the two species have the same atomic size. Therefore, despite the concentration gradient through the material, there are no potential gradients to influence the diffusion. In addition, both the equilibrium concentration of vacancies and also the frequency with which atoms jump into adjacent vacancies remain invariant with composition.

Consider then a system like the one described with a one dimensional concentration gradient of tracer. Further consider two adjacent atomic planes perpendicular to the direction of the concentration gradient at x_1 and x_2. The number of tracer atoms jumping from x_1 to x_2 in unit time (n^*_{12}) is given by:-

$$n^*_{12} = K.Pv.V.n^*_1 \tag{7}$$

where

K = Number of nearest neighbour sites which an atom in plane x_1 has in plane x_2.

Pv = Probability that a given nearest neighbour site is vacant

= N_v (i.e. the fraction of vacant sites in the lattice)

W = Average frequency with which an atom jumps into an adjacent vacant site.

n^*_1 = Number of tracer atoms in plane x_1.

similarly

$$n^*_{21} = K{\cdot}Pv{\cdot}W.n^*_2 \tag{8}$$

where

n^*_2 = Number of tracer atoms in plane x_2.

Since it is tracer diffusion that is under consideration, it is reasonable to assume that K, Pv and W are independent of composition. However, when dealing with alloys, the species present are not chemically identical and so this assumption is not valid.

From equations (7) and (8), the net number of tracer atoms flowing from x_1 to x_2 per unit time is:-

$$(n^*_{12} - n^*_{21}) = K.N_v.W\ (n^*_1 - n^*_2) \tag{9}$$

The concentration of tracer atoms in any plane, x_i, is the total mass of tracer in the plane divided by the volume occupied by all the atoms in the plane:-

$$C_i^* = \frac{n_i^*.M^*}{a.A} \tag{10}$$

Where,

M^* = Atomic weight of tracer.

a = Interatomic spacing and hence also the width of the atomic planes.

A = Area of atomic planes.

Eliminating n_i^* between equations (9) and (10) gives:-

$$(n_{12}^* - n_{21}^*) \frac{M^*}{A} = K.N_v.W.a.(C_1^* - C_2^*) \tag{11}$$

Now, the left hand side of equation (11) is the net mass of tracer atoms flowing in the +x direction per unit time through unit cross sectional area, which is defined as the diffusion flux (J). Further, $(C_1^* - C_2^*)$ can be replaced by means of the relationship:-

$$\frac{\partial C}{\partial x} = \frac{(C_2^* - C_1^*)}{a}$$

Thus, equation (11) becomes:-

$$\underline{\underline{J = -D \cdot \frac{\partial C}{\partial x}}} \tag{12}$$

Where

$$\underline{\underline{D = K.N_v.W.a^2}} \tag{13}$$

Thus, starting with some knowledge concerning the mechanism of diffusion, it has been possible to show that the diffusion flux is directly proportional to the negative concentration gradient. The proportionality constant (D) is called the diffusion coefficient, or diffusivity, and for the example of tracer diffusion it really is constant because all the factors in equation (13) are constant. D is not constant with composition in alloys however because many of the assumptions made in arriving at equation (13) cease to be valid.

3.4 Refinements to the Mechanistic Interpretation of D

It is possible to extend the above description of diffusion to deal with dilute binary alloys.

In the case of interstitial alloys, the solute atoms diffuse on a sub-lattice whose sites are essentially all vacant. Because of the sharp distinction between the sites which may be occupied by solvent atoms and those which can only accommodate solute atoms, the theoretical treatment of interstitial diffusion is relatively uncomplicated.

In a dilute substitutional alloy, however, solute and solvent atoms occupy sites on the same lattice and this makes it very much more difficult to derive an expression for the diffusion coefficient in terms of atomic parameters. In a dilute alloy, it is not unreasonable to neglect chemical interactions between the two different atomic species present. However, there are two other factors omitted from the mechanistic treatment of tracer diffusion which must be included in a description of substitutional alloys.

The first of these is that, in an alloy, the jump frequencies of the solute and solvent atoms may differ. This has been analysed [13] in terms of the effect of solute atoms on the electronic size distribution surrounding the ion cores which make up the lattice, and also

[14,15] by considering the mechanical stresses induced by the different sizes of solute and solvent atoms. However, there is no unified theory to account for the simultaneous operation of electronic and size effects.

The second factor which must be taken into account when dealing with alloys is Correlation between successive atomic jumps.

Consider firstly the jumps of a vacancy moving through a pure metal. After any jump, all the neighbours of the vacancy are identical so it shows no preference in the direction of its next jump. The jumps are therefore said to be uncorrelated or completely random, so the mean square distance ($\overline{r_v^2}$) travelled by the vacancy after n jumps of distance a is given by na^2, from equation (6).

Consider now a tracer atom diffusing by a vacancy mechanism in a pure metal. After any jump of the tracer atom, its neighbours are not all identical, one of them being a vacancy. This influences the probabilities of the various directions in which the tracer atom could move on its next jump. In fact, the tracer atom will have a greater tendency to jump back in the direction from whence it came then it does to continue in the same direction as its previous jump. Therefore, jump directions are correlated and not entirely random. The effect of this is that the mean square distance ($\overline{r_*^2}$) travelled by the tracer atom after n jumps of distance a is less than na^2 because the direction of a given jump has a greater than random tendency of cancelling out the previous jump. The degree of correlation in a particular structure is given by the correlation factor (f), which is defined as:-

$$f = \lim_{n \to \infty} \frac{\overline{r_*^2}}{\overline{r_v^2}} \qquad (14)$$

Taking account of correlation, equation (13) should actually read:-

$$D = f \cdot K.Nv \cdot W \cdot a^2 \qquad (15)$$

where f is less than unity for diffusion by a vacancy mechanism. It can be shown [16] that for tracer diffusion, f is approximately unity and so correlation effects can be conveniently ignored, but this is not the case for alloys where correlation effects are often of prime importance in determining the diffusion coefficients of the various atomic species.

3.5 Breakdown of Mechanistic Approach

Without having gone into much detail, it is clear that, even in the relatively simple case of a dilute binary substitutional alloy, a complete understanding of diffusion coefficients in terms of mechanism is very involved. In fact, it is quite unrealistic to attempt a complete mechanistic description of diffusion in more concentrated alloy systems where chemical interactions are important. It is, therefore, necessary to consider the problem of how to analyse diffusion phenomena in systems such as these where the mechanistic approach is too complex to be of any use. The answer to the dilemma is to treat the problem phenomenologically, by which means it is possible to deal with the type of system met in practice, containing several components and possibly more than one phase.

However, even within the context of a phenomenological theory, it is important to be aware of the mechanistics of diffusion, because there are two factors which prevent a solid metal from being treated as an amorphous mass.

The first of these is <u>Anisotropy</u>, which provides the opportunity for diffusion behaviour to vary with the direction of measurement. Extending the one dimensional derivation of the basic diffusion equation (12), the most general relationship that can be written for the flux components in a system containing a three dimensional concentration gradient is as follows:-

$$\underline{J_x} = - Dxx \cdot \frac{\partial C}{\partial y} - Dxy \cdot \frac{\partial C}{\partial y} - Dxz \cdot \frac{\partial C}{\partial z}$$

$$\underline{J_y} = - Dyx \cdot \frac{\partial C}{\partial x} - Dyy \cdot \frac{\partial C}{\partial y} - Dyz \cdot \frac{\partial C}{\partial z}$$

$$\underline{J_z} = - Dzx \cdot \frac{\partial C}{\partial x} - Dzy \cdot \frac{\partial C}{\partial y} - Dzz \cdot \frac{\partial C}{\partial z}$$

However, the nine coefficients defined above are not always all significant. For the cubic, tetragonal, orthorhombic and hexagonal structures, all the coefficients of the type Dij (where i and j are not equal) are zero. Further, for structures with cubic symmetry, all the cubic directions (i.e. ⟨100⟩ type) are identical and hence:-

$$Dxx = Dyy = Dzz$$

Now, $\underline{J} = \underline{Jx} + \underline{Jy} + \underline{Jz}$

Thus, for the cubic structures described above:

$$\underline{J} = - Dxx \frac{\partial C}{\partial x} + \frac{\partial C}{\partial y} + \frac{\partial C}{\partial z}$$

$$\underline{J} = - D_\circ \nabla C \tag{16}$$

Thus, provided it is a cubic structure that is under consideration, the isotropy requirement of the phenomenological approach is satisfied. In non-cubic structures, all directions are no longer equivalent, but, provided the degree of anisotropy is small, the directional dependency of diffusion properties may be neglected in polycrystalline materials whose grains are randomly oriented and small compared with the overall dimensions of the samples. However, to have small grains implies having many grain boundaries which themselves disturb the uniformity of the crystal lattice and thereby add a further complication to the phenomenological treatment. This introduces the second of the features of a solid metal which prevent its structure being ignored with respect to diffusion, i.e. Structural Defects.

(a) Point Defects

Point defects, whose presence and mobility are essential to the process of diffusion, do not invalidate the use of a phenomenological theory providing that their concentration remains at its equilibrium value, as defined by equation (2). Thus, the applicability of such a theory is confined to materials which have not been subjected to quenching, cold work or irradiation, each of which can produce a non-equilibrium distribution of point defects in a system. In practice, at the high temperatures at which most diffusion experiments are carried out, small departures from equilibrium of point defect concentrations are quickly rectified by the available sources and sinks. If, however, the specimen has previously been subjected to conditions which have produced a large excess of vacancies, voids can be formed on annealing by vacancy condensation. (N.B. The energetics render vacancies the more important category of point defects in close packed substitutional metals)

Another situation in which the point defect concentration can be distrubed from equilibrium is where the redistribution of two or more chemically different atomic species is taking place in a substitutional alloy system. If there is an imbalance of the fluxes across some interface in the system, then there is a net flow of matter across the interface, which results in an excess of vacancies on the side which is losing material and vice versa, assuming that diffusion occurs by a vacancy mechanism. If the flux imbalance is so large that the available sinks cannot cope with the vacancy excess, then voids can form. This phenomenon is known as Kirkendall porosity, having been discovered by Smigelskas and Kirkendall [9].

It has been suggested by Manning [17,18,19,20,21,22,23] that, even in the absence of Kirkendall porosity, the diffusion process is affected by a vacancy wind whenever a flux imbalance occurs. It is suggested that not all lattice sites are immediately adjacent to a vacancy source/sink and so a flux imbalance creates a flow of vacancies, or vacancy wind, in the opposite direction to the net flow of material. The flux of any given atomic species would be affected by the vacancy wind, but the vacancy wind depends on the overall motion of all the atoms, so the flux of a given species depends indirectly on the chemical potential gradients of all the species present.

Dayananda [24] has adapted his earlier work on "Atomic Mobilities in Multicomponent Diffusion" [25] to take account of vacancy wind effects. However, acceptance of these ideas has not been universal, since the evidence of the various attempts to verify the existence and importance of vacancy wind effects [26,27,28,29,30,31] have proved somewhat inconclusive.

In their kinetic analyses of diffusion in a concentration gradient, Le Claire [32] and Lane and Kirkaldy [33] followed the example set by Darken [34] in assuming that the vacancy concentration remains at equilibrium throughout an inhomogeneous system undergoing diffusion. Furthermore, Kirkaldy and Lane [35] have convincingly defended this assumption.

The problems thrown up by the potential existence of a vacancy wind are only important in connection with the determination of intrinsic diffusion coefficients. These characterise the individual fluxes of the different atomic species present in an alloy system, as opposed to interdiffusion coefficients which describe the overall diffusion process.

(b) High Diffusivity Paths

Although vacancies are the only thermodynamically stable defects in a solid metal, other types of structural imperfections, which remain in existence for kinetic reasons, are invariably present. Even a well annealed piece of metal contains a dislocation density of approximately

10^6 cm^{-2} [36], while a polycrystalline specimen also contains grain boundaries, which are regions of misorientation in the crystal lattice. In addition, the uniformity of the structure is disturbed by the presence of free surfaces whose effect on the diffusion process is likely to depend on the size and shape of the specimen under consideration.

In the regions of the metal where these various defects occur, the regular close packing of the atoms is disturbed in some way, which results in a relatively "open" structure compared with that of the perfect lattice. The result of this is that the diffusion coefficients pertaining to these defects are higher than the values characteristic of the perfect lattice. Hence, such defects are called High Diffusivity Paths.

Because atoms move at different speeds along different routes through a piece of metal, the observed diffusion flux results from the combined effect of the fluxes along each of these routes and is essentially a measure of the average flow of matter through any randomly chosen unit cross section. The contribution to the total flux from any one of the diffusion routes depends on the relevant value of the diffusion coefficient and also on the fraction of the total number of atoms occupying sites lying on that route. Now, it so happens that the contributions from the various routes differ by orders of magnitude from one another and therefore, in general, the overall diffusion flux is completely dominated by the process making the largest contribution. Thus, the observed diffusion coefficient (D) equals the characteristic coefficient of the dominant process.

The dependence of diffusion coefficient on temperature varies from one process to another and it has been shown [37] that as the temperature varies the dominant diffusion process changes. The transition temperatures between processes are found to be approximately constant for all metals if they are expressed as a fraction of the metal's melting point (T_m) in degrees :-

When,	$T_m > T > 2T_m/3$	lattice diffusion dominates
	$2T_m/3 > T > T_m/2$	grain boundary diffusion dominates
	$T_m/2 > T$	dislocation diffusion dominates

Therefore, experiments conducted at temperatures above two thirds of the melting point of the system under consideration will yield diffusion data characteristic of lattice diffusion, and so on. Surface diffusion does not, in general, make a significant contribution to the diffusion flux in metal specimens of the size and shape normally employed in diffusion experiments.

In any comparison between the diffusion behaviour of one system with another, it is important to ensure that the dominant diffusion process is the same in each case, otherwise the comparison is of little value. Thus, the temperature ranges over which such comparative studies may be made are often quite limited, this being another piece of information which does not arise from the general phenomenological theory.

4. PHENOMENOLOGICAL TREATMENT OF DIFFUSION

4.1 Binary Systems

A considerable knowledge of the structure of a solid metal and the mechanism of diffusion was required in order to derive an equation for the diffusion flux in an isothermal, isobaric, one dimensional binary system (equation (12)). However, as early as 1855, Adolf Fick [1] observed that in any inhomogeneous single phase system matter tends to flow so as to reduce concentration gradients, and thus arrived at equation (12) intuitively, prior to any experimental work in diffusion.

Fick's 1st. Law, as this earliest formulation of diffusion behaviour is called, is essentially a static law, but a dynamic variant can be derived from it:-

$$\underline{\underline{\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D\,\frac{\partial C}{\partial x}\right]}} \qquad (17)$$

This dynamic equation, which relates the variation of concentration with time at any point to the concentration gradient, is Fick's 2nd. Law.

Fick's 1st. and 2nd. Laws can easily be extended to cope with diffusion in more than one dimension as shown by equation (16). However, for isotropic systems all dimensions are equivalent, so for ease of presentation only the one dimensional equations will be considered here.

The factor D in Fick's Laws was originally introduced as a proportionality constant, but it was later demonstrated for the diffusion of electrolytes by Clack [38] and for metallic systems by Mehl [39] that in general diffusion coefficients are not constant, but are functions of composition.

Much of the theoretical work in diffusion is associated with solving Fick's 2nd Law for various boundary conditions. This is relatively straightforward for the case of binary systems in which D is assumed to be independent of composition, and Crank [40] has provided a comprehensive listing of the various solutions available. If D is not independent of composition, however, then it is a function of distance and cannot be taken outside the differential in Fick's 2nd. Law, which is consequently rendered inhomogeneous and unable to be directly integrated. However, Boltzmann [41] showed that x and t in equation (17) can be replaced by a single variable, $\lambda = x/\sqrt{t}$:-

$$-\frac{\lambda}{2} \cdot \frac{dC}{d\lambda} = \frac{d}{d\lambda}\left[D \cdot \frac{dC}{d\lambda}\right] \tag{18}$$

This is now an ordinary homogeneous differential equation between C and λ. It is important to note, however, that this transformation of x and t into λ and equation (18) can only be used in situations where the boundary conditions are expressable in terms of λ alone.

For example, consider the diffusion couple defined by the following boundary conditions :-

$C_i = C_i^-$ at $x < 0$, $t = 0$; and at $x \rightarrow -\infty$, $t > 0$

$C_i = C_i^+$ at $x > 0$, $t = 0$; and at $x \rightarrow +\infty$, $t > 0$

Where i refers to any one of the components of the system. These conditions could also be expressed as :-

$$C_i = C_i^- \text{ at } \lambda = -\infty \qquad (19)$$

$$C_i = C_i^+ \text{ at } \lambda = +\infty \qquad (20)$$

Thus, since x and t are not involved separately, equation (18) can be employed.

Kirkaldy, Lane and Mason [42] derived the following iterable solution to equation (18), which is rapidly convergent even when D varies strongly with C :-

$$C = k_2 + k_1 \int_{\lambda}^{\infty} \frac{1}{D} \exp\left[- \int_{0}^{\lambda} \frac{\lambda}{2D} \cdot d\lambda \right] \cdot d\lambda \qquad (21)$$

where k_1 and k_2 are constants of integration.

However, of greater interest here is an alternative integral of equation (18) which was noted by Boltzmann [41]. For the case of an infinite diffusion couple, as defined by the boundary conditions (19) and (20) above, equation (18) can be integrated (remembering that $dC/d\lambda = 0$ at $C = C^-$) to give:-

$$\underline{\underline{\frac{1}{2} \int_{C-}^{C} \lambda dC = -D \; \frac{dC}{D\lambda}_{\,C=C}}} \qquad (22)$$

where C throughout refers to the concentration of the dependent species.

Although it is not a solution to the diffusion equation, equation (22) can be used to determine the diffusion coefficient at any point along the concentration profile of an infinite diffusion couple. Since the concentration profile to be analysed is at a fixed time, then equation (22) can be written:-

$$-\frac{1}{2}\int_{C-}^{C} x\,dC = Dt\,\frac{dC}{dx}_{C=C} \qquad (23)$$

From a graph of the concentration profile, the concentration gradient can easily be measured at any point, and the integral, $\int_{C-}^{C} x\,dC$, can be determined by measuring the appropriate area under the curve. Errors in the value of D calculated using equation (23) are greatest where C is near the terminal compositions because in these regions $\int_{C-}^{C} x\,dC$ and dC/dx are both very small.

An important point to notice is that the determination of $\int_{C-}^{C} x\,dC$ by measuring the area under the curve requires knowledge of the position of x=0. This may be found by considering equation (23) at $C=C^+$ where dC/dx = 0:-

$$\int_{C^-}^{C^+} x\,dC = 0 \qquad (24)$$

The interface defined in this way is called the Matano Interface after Chujiro Matano who first employed equation (23) to determine diffusion coefficients in metallic systems [43]. This technique of determining coefficients has since become known as the Boltzmann-Matano method.

Equation (23) is strictly only valid for a system which shows no volume change on mixing, but it can be modified to cope with systems where the variation of molar volume with composition is not negligible:-

$$-\frac{1}{2}\int_{C^-}^{C} \frac{x}{Vm}\,dC = \frac{Dt}{Vm}\,\frac{dC}{dx} \qquad (25)$$

where Vm = Molar volume.

In its original form, the Boltzmann-Matano technique was somewhat tedious, principally because of the need to locate the Matano Interface. However, equation (23) has been modified [44,45,46], such that the distance parameter only appears in differential form, thus obviating the need to locate its origin. Using the same format as before, the modified form of equation (23) is :-

$$(1-Y) \int_{-\infty}^{x} (C-C^{-})\, dx + Y \int_{x}^{+\infty} (C^{+}-C)\, dx = 2Dt \left.\frac{dC}{dx}\right._{C=C} \qquad (26)$$

Molar volume is here assumed to be constant, and the differential of C with respect to x is written as a perfect differential since t is assumed to be constant.

The factor Y in equation (26) is defined as follows:-

$$Y = \frac{C-C^{-}}{C^{+}-C^{-}}$$

4.2 Reference Frame for Diffusion

Until the 1940's, it was assumed that the reference frame for diffusion was fixed relative to the external geometry of the system and so distance measurements could be made from any point fixed with respect to that geometry. Thus for the case of metallic diffusion couples, comprising welded pairs of alloys, the origin for measurements was considered to be fixed at the position of the original interface.

Now, at this time the direct exchange mechanism was the established idea for diffusion in substitutional metallic alloys and hence it was assumed that the amount of component 1 diffusing in one direction in a given time was the same as the amount of component 2 diffusing in the reverse direction in the same time. This idea is not only consistent with the concept of the Matano Interface, which consequently had considerable intuitive appeal at the time, but also predicts that the Matano Interface is coincident with the position of the original interface between the welded pair, in the absence of molar volume changes on mixing.

The first attack on these mutually consistent ideas of substitutional diffusion in binary metal alloys was aimed at the concept of the direct exchange mechanism. This was led by Huntington and Seitz [6,7], who showed that the vacancy diffusion mechanism, which permits the two components to move at different speeds, is energetically much more favourable than the direct exchange mechanism. Now, if material flows in one direction in a diffusion couple faster than it does in the other, then the side enjoying a nett receipt of material will expand at the expense of the other. Therefore the interface between the two sides of the couple will move relative to an external reference point. The only way to observe such an effect is to incorporate into the system an internal reference frame of some kind and then to monitor this relative to the external frame. This experiment was first carried out by Hartley [47] who studied the motion of inert titanium dioxide markers in the diffusion of acetone in cellulose acetate. However, it was Smigelskas and Kirkendall [9], who first brought the concept to the attention of the metallurgical world with their observation of the motion of inert molybdenum wires in diffusion couples between copper and α brass.

The value of making diffusion measurements relative to an internal frame of reference was first recognized by Darken [34], who showed that it was thus possible to evaluate two different diffusion coefficients for a binary system characterising the respective motions of the two different atomic species. These were later called Intrinsic Diffusion Coefficients by Hartley and Crank [48], who arrived at the same conclusions as Darken in an independent treatment of this subject.

Considering one dimension only, the flux of component 1 as measured in an external reference frame (J_1) comprises two elements:-

a) That by diffusion, which is relative to local inert markers and is given by Fick's 1st Law:-

$$- D_1 \frac{\partial C_1}{\partial x}$$

b) That in common with local inert markers, which travel at an externally measured velocity of v (a function of position (x) and time (t)):-

Thus, C_1v

$$J_1 = \left[- \frac{D_1 \partial C_1}{\partial x} - C_1 v\right] \qquad (27)$$

Conversion to a Fick's 2nd. Law - type expression gives:-

$$\frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x} \left[\frac{D_1 \partial C_1}{\partial x} - C_1 v\right] \qquad (28)$$

and by analogy

$$\frac{\partial C_2}{\partial t} = \frac{\partial}{\partial x}\left[\frac{D_2 \partial C_2}{\partial x} - C_2 v\right] \tag{29}$$

Assuming that the concentrations, C_1 and C_2, represent atomic fractions:-

$$C_1 + C_2 = 1$$

$$\frac{\partial C_1}{\partial t} + \frac{\partial C_2}{\partial t} = 0$$

Hence addition of equations (28) and (29) gives:-

$$\frac{\partial}{\partial x}\left[D_1 \frac{\partial C_1}{\partial x} + D_2 \frac{\partial C_2}{\partial x} - v\right] = 0$$

Integrating:

$$D_1 \frac{\partial C_1}{\partial x} + D_2 \frac{\partial C_2}{\partial x} - v = I \tag{30}$$

where I is a constant of integration.

Now, at very great distances from the initial interface of the binary diffusion couple, $\partial C_1/\partial x$ and $\partial C_2/\partial x$ are zero.

$$V_{\text{At } x=\infty} = I \tag{31}$$

By fixing the co-ordinate frame such that the x axis is fixed relative to the ends of the couple, V_∞ is zero. Therefore, from equation (31):

$$I = 0$$

Equation (30) becomes:

$$V = D_1 \frac{\partial C_1}{\partial x} + D_2 \frac{\partial C_2}{\partial x} \tag{32}$$

Substitute for V in equation (28):-

$$\frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x}\left[(1-C_1)\, D_1 \frac{\partial C_1}{\partial x} - C_1 D_2 \frac{\partial C_2}{\partial x}\right] \qquad (33)$$

Now, $1 - C_1 = C_2$

and $\frac{\partial C_2}{\partial x} = -\frac{\partial C_1}{\partial x}$

$$\frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x}\left[(C_2 D_1 + C_1 D_2)\frac{\partial C_1}{\partial x}\right] \qquad (34)$$

Substitute $\lambda = x/t^{1/2}$

$$-\frac{1}{2}\lambda\, dC_1 = d\left[(C_2 D_1 + C_1 D_2)\frac{dC_1}{d\lambda}\right] \qquad (35)$$

Since x and t have disappeared from equation (35) then $C_1 = f(\lambda)$ is the solution to equation (34) provided the boundary conditions are satisfied. To meet this condition the origin must be selected as the position of the initial interface of the diffusion couple. This is so because at t=0, $\lambda = \infty$ at all positive values of x, and $\lambda = -\infty$ at all negative values of x. Therefore, unless x=0 corresponds to the step change in concentration, then $\lambda = \infty$ does not correspond to a single value of C_1, i.e. $C_1 \neq f(\lambda)$.

Integrating equation (35) from $\lambda = -\infty$, where $C_1 = C_1^-$ and $dC_1/d\lambda = 0$, to a point of interest where $C_1 = C_1$:-

$$C_2 D_1 + C_1 D_2 = \frac{-\frac{1}{2}\int_{C_1^-}^{C_1} \lambda\, dC_1}{dC_1/d\lambda} \qquad (36)$$

Now, from equation (22), this expression can be seen to be equal to D, the single coefficient describing the overall diffusion process as measured in the Boltzmann-Matano method.

$$\text{i.e.}\quad \underline{\underline{D = C_2D_1 + C_1D_2}} \tag{37}$$

where C_1 and C_2 are atom fractions of components 1 and 2, respectively.

Hence, it is seen that the, so called, interdiffusion coefficient D as measured in the Boltzmann-Matano method remains a valid description of the diffusion process, and comprises a weighted sum of the two intrinsic coefficients. To determine the intrinsic coefficients from the interdiffusion coefficient requires an additional relationship between the two unknowns, which is supplied by equation (32).

$$v = (D_1 - D_2)\frac{\partial C_1}{\partial x} = (D_2 - D_1)\frac{\partial C_2}{\partial x} \tag{38}$$

Thus by carrying out a diffusion experiment using inert markers, and by measuring the velocity of these markers in the same external reference frame as the measurement of the interdiffusion coefficient, the intrinsic coefficients can be found by simultaneous solution of equations (37) and (38).

Despite being described as intrinsic, such coefficients are not fundamental parameters of the elements to which they refer. From above, it is seen that intrinsic coefficients contain more information than interdiffusion coefficients, but they are no less dependent on composition. For most practical purposes, therefore, intrinsic coefficients are of no greater value as a means of describing diffusion behaviour than interdiffusion coefficients, which are easier to evaluate.

4.3 Multicomponent Systems

The theory of diffusion in binary systems has been described on the basis of Fick's Laws. It has long been recognized that diffusion coefficients as defined by Fick's Laws are functions of state variables such as composition. However, since D is always positive in binary systems, the general concept of Fick's Laws that the driving force for diffusion of a species is the concentration gradient of that species (in the absence of temperature, pressure and electric potential gradients) was considered to hold true in metallic systems until systems of more than two components started to be studied in the 1940s.

Even before this time, however, diffusion in non-metallic systems had been related to chemical potential rather than concentration gradients. The groundwork was laid by Nernst [49] in 1888 who expressed the driving force for diffusion between liquid solutions of different compositions in terms of osmotic pressure, which is directly related to the chemical potential. Much later, in 1932, Onsager and Fuoss [50] related the diffusivity, mobility and activity coefficient in aqueous solutions, producing results which were confirmed experimentally by Harned and Nuttall [51]. The concept that chemical potential or activity gradients are the driving forces for diffusion was belatedly applied to metallic systems by Darken [52] who later [53] answered scepticism with experimental evidence of "uphill" diffusion in a number of ternary metallic systems. Darken looked at four diffusion couples between steels of different compositions. Of these, one in particular has become famous as the "Darken Couple", which comprised the two alloys:

Fe 0.478%C 3.80%Si ——— Fe 0.441%C.

Following a diffusion anneal, the resultant carbon concentration profile was determined and is reproduced in Figure 2, from which it is seen that although the carbon concentration was initially approximately uniform right across the couple, carbon has diffused away from the silicon containing side of the couple to produce what appears to be a step change in carbon concentration.

In fact, there is not really a discontinuity in the carbon concentration profile, but the gradient at the interface is very steep because the substitutional silicon diffuses much slower than the interstitial carbon, so that on the scale of Fig. 2 the initial step change in silicon concentration at the original junction of the couple has been removed to an imperceptible degree. However, the fact remains that the initially uniform carbon concentration has created a concentration gradient by diffusion and carbon has continued to diffuse up that gradient. The reason for this is that the presence of silicon in the steel increases the chemical potential of carbon. Therefore, although there is initually no carbon concentration gradient in the couple, there is a carbon activity gradient and it is the latter which provides the driving force for diffusion.

This example of the Darken Couple illustrates clearly the extent of the interaction between chemically different species in a system. It is, therefore, apparent that the application of Fick's 1st. Law directly to ternary (and higher) systems, by simply writing the flux of each component to be proportional to the negative of its own concentration gradient, is not very satisfactory. Hence, a rethink of the basic phenomenological equations of diffusion is required.

Phenomenological Equations of Multicomponent Diffusion

If a force is applied to a body then the body accelerates in the direction of the force (Newton's 2nd. Law of Motion). If, however, the motion of the body generates a retarding force, which increases with velocity, then eventually the applied and retarding forces will become equal at which point the velocity of the body will stabilize.

Where the body in motion is a diffusing atom, it is assumed that the retarding force, which is equal and opposite to the applied force in the steady state, is proportional to the velocity of the atom. To the authors' knowledge, this assumption remains neither confirmed nor contested, with the result that it has come to be accepted as self-evident by workers in the diffusion field. However, in the mathematically analagous field of viscosity (where transport of momentum rather than mass is the concern), it is known that so called Non-Newtonian Fluids exist in which the viscosity is a function of the applied stress and hence the momentum gradient. Examples include Bingham Fluids, many of which show thixotropy (e.g. Non-drip paints). Nevertheless, the proportionality between diffusion flux and applied force will be accepted here. The velocity per unit force is called the mobility (B) of the species.

Thus for the simple case where a species (i) is acted upon by a single force (F_i), then the flux (J_i) can be written:-

$$J_i \propto F_i$$

Now any force can be written as a negative potential gradient, therefore assuming that π is the relevant potential field:-

$$J_i \propto - \nabla\pi$$

If attention is focussed on the single dimension x:-

$$J_i = -M_{i\pi} \cdot \frac{\partial\pi}{\partial x} \qquad (39)$$

where $M_{i\pi}$ is the proportionality constant or coefficient. However, in general the atomic species of a system are subjected to more than one potential field.

The term flux can be interpreted as the rate at which a system returns to equilibrium having been distrubed therefrom. Therefore, the potentials which contribute to the flux are those which describe the thermodynamic equilibrium of a system, that is:- Temperature (T), Pressure or Mechanical Stress (P), Electric or other scalar potential ($\emptyset$) and the Chemical Potentials ($^{\mu}i$) of all the different atomic species present. Chemical potential is defined as the partial molar Gibbs Free Energy:-

$$\mu_i = \left[\frac{\partial G}{\partial n_i}\right]_{P,\ T,\ n_j} \qquad i \neq j$$

Where G = Gibbs Free Energy of the subsystem or phase

n_i = Number of moles of component i.

Thus from Eq. (39), the most general equation for the flux of component i in an n component system is:-

$$J_i = -M_{i1}\frac{\partial \mu_1}{\partial x} - M_{i2}\frac{\partial \mu_2}{\partial x} \ldots - M_{in}\frac{\partial \mu_n}{\partial x} - M_{iT}\frac{\partial T}{\partial x} - M_{iP}\frac{\partial P}{\partial x} - M_{i\phi}\frac{\partial \phi}{\partial x} \qquad (40)$$

For ease of presentation an isothermal, isobaric and isoelectric-potential system will be considered here, so the last three terms of Eq. (40) go to zero. However, if the vacancy diffusion mechanism is to be assumed then a term to take account of the vacancy potential gradient must be included:-

$$J_i = -\sum_{j=1}^{n} M_{ij}\frac{\partial \mu_j}{\partial x} - M_{iv}\frac{\partial \mu_v}{\partial x} \qquad (41)$$

Equations of this form exist for the fluxes of each of the n species, while an analogous equation exists for the vacancy flux:-

$$J_v = -\sum_{j=1}^{n} M_{vj}\frac{\partial \mu_j}{\partial x} - M_{vv}\frac{\partial \mu_v}{\partial x} \qquad (42)$$

There are thus (n+1) equations containing $(n+1)^2$ M coefficients. However, it is possible to reduce these numbers by considering the existence of dependences between the fluxes, and also between the coefficients.

Firstly it is assumed that the total number of lattice sites is conserved, in which case the net current of sites must vanish:-

$$J_v + \sum_{i=1}^{n} J_1 = 0 \tag{43}$$

Consider equations (41) for i=1 to n and equation (42), and further consider that all the potential gradients are zero except for $\partial\mu_1/\partial x$. Application of equation (43) then gives:-

$$M_{v1} + \sum_{i=1}^{n} M_{i1} = 0.$$

Therefore, by extension it is seen that if equations (41) and (42) are to be valid for all values of the chemical potential gradients, then equation (43) dictates that :-

$$M_{vj} = - \sum_{i=1}^{n} M_{ij} \qquad j = 1 \text{ to } n \tag{44}$$

$$M_{vv} = - \sum_{i=1}^{n} M_{iv} \tag{45}$$

Another set of relationships between the M coefficients is obtained by invoking Onsager's concept of microscopic reversibility [54,55] which states that for a system in thermodynamic equilibrium every type of micromotion occurs just as often as its reverse. The consequences of this are that the M coefficients described above form a symmetrical matrix:-

$$M_{ij} = M_{ji} \text{ for all i and j} \tag{46}$$

$$M_{iv} = M_{vi} \text{ for all i} \tag{47}$$

The application of equations (43) to (47) inclusive results in a simplification of the flux equations to :-

$$J_i = - \sum_{j=1}^{n} M_{ij} \cdot \frac{\partial(\mu_j - \mu_v)}{\partial x} \qquad i = 1 \text{ to } n \tag{48}$$

Now, if it is assumed that the concentration of vacancies is maintained in local equilibrium, then $\mu_v = 0$ and so:-

$$J_i = - \sum_{j=1}^{n} M_{ij} \cdot \frac{\partial \mu_j}{\partial x} \qquad i = 1 \text{ to } n \tag{49}$$

The question of whether vacancies are able to equilibrate with the lattice throughout the system has been discussed earlier. It was Mainning [17-23] who first suggested that μ_v should not be assumed to be zero at all points in a system, in connection with his work on the "Vacancy Wind". However, the idea has not been universally accepted.

The assumption is usually made that the cross coefficients in equation (49) (M_{ij}, $i \neq j$) are zero.

$$\text{i.e. } J_i = -M_{ii} \frac{\partial \mu_i}{\partial x}, \qquad i = 1 \text{ to } n \tag{50}$$

This implies that the flux of a given species in a system is dependent only on the chemical potential gradient of that species. However, this would not be true if Manning's theories are correct. His vacancy wind would have a correlation effect on the motion of atoms in the system, but the vacancy wind would be a consequence of the fluxes of all the diffusing species. Therefore, by a second order effect, the diffusion flux of each species would depend on all the chemical potential gradients. However, it will be assumed here that this effect, if real, is negligibly small, such that equation (50) is a good approximation.

Practical Diffusion Equations

Equation (50) describes diffusion fluxes in terms of chemical potentials, and it is valid irrespective of the number of components in the system. However, it suffers from the disadvantage that chemical potential gradients are inherently difficult to measure, and so if the scope for experimental work in multicomponent systems is not to be severely restricted the chemical potential term in equation (50) must be replaced by more amenable parameters.

(a) Binary Systems

A practical diffusion equation has already been described for binary systems, that is Fick's 1st. Law which relates the flux of a species to its concentration gradient - equation (12).

The fact that two independent flux equations exist ((12) and (50)) for binary systems enabled Darken [34] to produce a relationship between the intrinsic diffusion coefficient (D_i) of a species (i) in a binary system and its activity coefficient (γ_i).

$$\text{i.e.}: \quad D_i = B_i\, RT \quad [1 + Ni \frac{d \ln \gamma_i}{dN_i}] \qquad i = 1,2 \qquad (51)$$

Where, B_i = Mobility of i, as defined earlier.

R = Gas Constant (i.e. Boltzmann's Constant x Avagadro's Number)

T = Temperature K

N_i = Mole Fraction of i

The activity coefficient is defined as:-

$$\gamma_i = \frac{a_i}{N_i}$$

where a_i is the activity of component i and is related to its chemical potential as follows:-

$$\mu_i = \mu_i^o + RT \ln a_i$$

Where μ_i^o is the chemical potential of i in its reference or standard state. When the species is in its standard state, its activity is unity.

If the activity coefficient of a species in a solution is independent of composition then equation (51) becomes:-

$$D_i = B_i RT \qquad (52)$$

This equation was first formulated by Einstein [56], but it is seen here to be true only when γ_i is constant. This condition prevails only in an ideal solution ($\gamma_i = 1$) or in a solution which is sufficiently dilute that the activity of the solute obeys Henry's Law (i.e. Activity α Concentration) while that of the solvent obeys Raoult's Law (i.e. ideal behaviour).

It is rare for a metallic solution to even approach ideality, but many systems do approximate to, so called, regular behaviour [57] over wide ranges of composition. A regular solution is one for which the entropy of mixing is equal to the entropy of mixing of an ideal solution. For such a system it can be shown that:-

$$\ln \gamma_1 = \alpha N_2^2 \tag{53}$$

$$\ln \gamma_2 = \alpha N_1^2 \tag{54}$$

Where α is a constant.

By differentiation of equations (53) and (54):-

$$\frac{d \ln\gamma_1}{dN_1} = \alpha \cdot 2N_2 \cdot \frac{dN_2}{dN_1} = -2\alpha N_2 \tag{55}$$

$$\frac{d \ln\gamma_2}{dN_2} = \alpha \cdot 2N_1 \cdot \frac{dN_1}{dN_2} = -2\alpha N_1 \tag{56}$$

Substitution in equation (51) gives:-

$$D_i = B_i RT (1 - 2\alpha N_1 N_2) \qquad i = 1,2 \tag{57}$$

By means of equation (51) together with equation (37), Darken [34] went on to produce a relationship between the interdiffusion coefficient D for a binary system, as measured in a Boltzmann-Matano experiment, and the tracer diffusion coefficients of the two species:-

$$D = (N_1 D_2^* + N_2 D_1^*) \left[1 + N_i \frac{d \ln\gamma_i}{dN_i}\right] \tag{58}$$

Where i = 1 or 2, since from the Gibbs Duhem equation:

$$N_1 \frac{d \ln\gamma_1}{dN_1} = N_2 \frac{d \ln\gamma_2}{dN_2}$$

D_1^* and D_2^* are the diffusion coefficients as measured in a radioactive tracer experiment, which Darken showed to be virtually equivalent to the self diffusion coefficients of the two pure elements.

For a regular solution, equation (58) becomes:-

$$D = (N_1 D_2^* + N_2 D_1^*) (1 - 2\alpha N_1 N_2) \tag{59}$$

While for ideal or dilute (Henrian/Raoultian) solutions:-

$$D = N_1 D_2^* + N_2 D_1^* \tag{60}$$

(b) Multicomponent Systems

In developing a practical equation for multicomponent systems, equation (50) will be taken as the starting point. For the isothermal, isobaric, iso-electric potential system under consideration, the chemical potential of each species is a function of the only non-constant state variable, that is composition.

$$\mu_i = f\,(C_1, C_2, \ldots\ldots\ldots\ldots\, C_n)$$

$$\frac{\partial \mu_i}{\partial x} = \frac{\partial \mu_i}{\partial C_1} \cdot \frac{\partial C_1}{\partial x} + \ldots\ldots\ldots\ldots \frac{\partial \mu_i}{\partial C_n} \cdot \frac{\partial C_n}{\partial x} \qquad (61)$$

Substituting for $\partial\mu_i/\partial x$ from equation (61) into equation (50) gives:-

$$J_i = -M_{ii} \sum_{j=1}^{n} \frac{\partial \mu_i}{\partial C_j} \cdot \frac{\partial C_j}{\partial x}\,, \qquad i = 1 \text{ to } n \qquad (62)$$

Putting $$D'_{ij} = Mii \; \frac{\partial \mu_i}{\partial C_j}$$

$$J_i = -\sum_{j=1}^{n} D'_{ij} \frac{\partial C_j}{\partial x}\,, \qquad i = 1 \text{ to } n \qquad (63)$$

This is now a practical diffusion equation since the diffusion fluxes are related to concentration gradients which can usually be measured easily. For an n component system there are n equations of the form of (63), each containing n terms, therefore n^2 coefficients are required to describe such a system. However, dependencies exist between the concentration gradients and also between the fluxes which reduce the number of coefficients required.

The total of the concentrations of all the species must be constant:

$$\text{i.e.} \quad \sum_{j=1}^{n} C_j = \text{Constant}$$

$$\sum_{j=1}^{n} \frac{\partial C_j}{\partial x} = 0$$

$$\frac{\partial C_n}{\partial x} = - \sum_{j=1}^{n-1} \frac{\partial C_j}{\partial x}$$

$$D'_{in} \cdot \frac{\partial C_n}{\partial x} = - \sum_{j=1}^{n-1} D'_{in} \cdot \frac{\partial C_j}{\partial x} \tag{64}$$

Now, equation (63) can be re-written:-

$$J_i = - \sum_{j=1}^{n-1} D'_{ij} \frac{\partial C_j}{\partial x} - D'_{in} \frac{\partial C_n}{\partial x}$$

Substitute from equation (64):-

$$J_i = - \sum_{j=1}^{n-1} D'_{ij} \frac{\partial C_j}{\partial x} + \sum_{j=1}^{n-1} D'_{in} \frac{\partial C_j}{\partial x}$$

$$J_i = - \sum_{j=1}^{n-1} D_{ij} \frac{\partial C_j}{\partial x}, \quad i = 1 \text{ to } n \tag{65}$$

Where $D_{ij} = D'_{ij} - D'_{in}$

Thus, each equation now contains only (n-1) terms. Further, by defining an appropriate fundamental reference frame, one of the fluxes can be made dependent so that only (n-1) diffusion equations are required containing $(n-1)^2$ coefficients. Examples of fundamental reference frames which have been used include [58]:-

i) Mass Fixed frame - which is defined to be fixed relative to the moving centre of mass of the system, so that the sum of all the fluxes is zero.

ii) Solvent fixed frame - which is defined such that there is no net flux of solvent.

iii) Volume fixed frame - in which fluxes are measured with respect to the local centre of volume.

The values of the diffusion coefficients in the now (n-1) equations of the form of equation (65) depend on the particular flux which has been selected as the dependent one. Therefore for clarity, the species whose flux is dependent is usually written as a superscript to the diffusion coefficients. Assuming the flux of component n to be dependent:-

$$J_i = - \sum_{j=1}^{n-1} D^n_{ij} \cdot \frac{\partial C_j}{\partial x}, \qquad i = 1 \text{ to } n-1 \tag{66}$$

This is the practical diffusion equation sought and is the multicomponent version of Fick's 1st. Law. The D^n_{ij} are interdiffusion coefficients and give a measure of the effect of the j concentration gradient on the diffusion flux of i, when the flux of n is considered dependent. When i = j, the D^n_{ij} are called Direct or On-Diagonal Coefficients, while when $i \neq j$, they are called Cross or Off-Diagonal Coefficients.

It is the existence of cross coefficients which provides the substantial intellectual jump between the understanding of diffusion in binary systems and that in ternary and higher order systems. It can be seen that when $n = 2$, equation (66) reduces to the original form of Fick's 1st. Law containing a single direct diffusion coefficient and no cross coefficients. Thus it is seen that for binary systems, the correct mathematical relationships are obtained by assuming the driving force for diffusion of a species to be its own concentration gradient. The additional feature inherent in systems of more than two components is the dependence of the diffusion flux of a species on the concentration gradients of all the other species and it is the cross diffusion coefficients which describe this effect. This reflects the fact that the driving force for diffusion of a species is actually its chemical potential gradient, which is a function of the concentration gradients of all the species present.

Dependencies between the Diffusion Coefficients

It was shown originally by Onsager [59], and later clarified by Hooyman [60] that application of the principle of Microscopic Reversibility [54,55] to the practical multicomponent diffusion equation (66) leads to dependencies amongst the D coefficients. Hence, in principle the number of D coefficients required to describe an n component system can be reduced to $n(n-1)/2$, e.g. For a ternary system there are three independent coefficients. However, to achieve this involves a re-introduction of the thermodynamic parameter, chemical potential.

This drawback can be overcome in dilute solutions, in which Henrian behaviour is shown by the solutes. In such circumstances, the variation of activity with composition is linear with the result that equations relating the D coefficients can be written in terms of concentrations [42]. For non-Henrian solutions, this simplification is not possible, so that in general the $(n-1)^2$ matrix of D coefficients is the minimum number needed to describe an n component system.

In addition to the above mentioned reference [42] the application of thermodynamic conditions to the allowed values of D coefficients is also considered in references [61, 62, 63].

A useful result of Kirkaldy, Weichert and Zia-Ul-Haq [63] is a set of conditions applicable to the values of the interdiffusion coefficients of a ternary system ABC assuming A to be the solvent:-

$$\begin{aligned} D_{BB} + D_{CC} &> 0 \\ D_{BB}\, D_{CC} - D_{BC}\, D_{CB} &\geqslant 0 \\ (D_{BB} + D_{CC})^2 &\geqslant 4\ (D_{BB}\, D_{CC} - D_{BC}\, D_{CB}) \end{aligned} \qquad (67)$$

These conditions result from purely thermodynamic considerations. However, kinetic constraints are also important (see for example [64]), and consideration of these in addition to the thermodynamic effects leads to the following more restrictive conditions on the values of the D coefficients:-

$$\begin{aligned} D_{BB} &> 0 \\ D_{CC} &> 0 \\ D_{BC}\, D_{CB} &\geqslant 0 \\ D_{BB}\, D_{CC} - D_{BC}\, D_{CB} &\geqslant 0 \end{aligned} \qquad (68)$$

For a ternary system, it is usually apparent which species is considered to be the solvent and so, as here, the superscript to the diffusion coefficients is frequently omitted.

Dynamic Multicomponent Diffusion Equation

Equation (66), like Fick's 1st. Law, is a static equation since it relates an instantaneous flux to a number of instantaneous concentration gradients. However, in the same way that Fick's 2nd. Law was derived from his first, so a dynamic version of equation (66) can be written to deal with non-steady state situations:-

$$\frac{\partial C_i}{\partial t} = \sum_{j=1}^{n-1} \frac{\partial}{\partial x} \left[D^n_{ij} \cdot \frac{\partial C_j}{\partial x} \right], \qquad i = 1 \text{ to } (n-1) \qquad (69)$$

Equation (69) is the most general form of diffusion equation for an isothermal, isobaric, iso-electric potential single phase system in which concentration gradients are uni-dimensional.

Solution of the Multicomponent Diffusion Equation

As it stands, equation (69) is inhomogeneous and consequently it cannot be solved except by numerical methods. However, if certain assumptions can be made concerning the ways in which the various diffusion coefficients vary with composition then there exists some scope for simplification.

(a) Solutions with Constant Coefficients

There are a number of conditions under which an analytical or iterable solution may be obtained for the diffusion equation when the coefficients are constant [65]. Attention here will be focussed on ternary systems, and of particular interest are the boundary conditions applicable to the infinite diffusion couple; these can be uniquely defined in terms of the parameter λ ($\lambda = x/t^{1/2}$) without involving either x or t separately. The boundary conditions, so defined, are given by equations (19) and (20).

Writing equation (69) for a ternary system ABC, with A specified as solvent, in terms of λ, assuming the diffusion coefficients to be independent of composition:-

$$\frac{-\lambda}{2} \frac{dC_B}{d\lambda} = D_{BB} \cdot \frac{d^2C_B}{d\lambda^2} + D_{BC} \cdot \frac{d^2C_C}{d\lambda^2} \qquad (70)$$

$$\frac{-\lambda}{2} \frac{dC_C}{d\lambda} = D_{CB} \frac{d^2C_B}{d\lambda^2} + D_{cc} \frac{d^2C_C}{d\lambda^2} \qquad (71)$$

Thus it is seen that the diffusion equations are now homogeneous with λ as the only independent variable and, since the boundary conditions for an infinite diffusion couple are defined in terms of λ alone, solutions of equations (70) and (71) will be unique for such a couple.

The complete solutions of equations (7) and (71) have been derived by Fujita and Gosting [66] and are reported below:-

$$C_B = a \operatorname{erf} \frac{\lambda}{2u^{1/2}} + b \operatorname{erf} \frac{\lambda}{2v^{1/2}} + c \qquad (72)$$

$$C_C = d \operatorname{erf} \frac{\lambda}{2u^{1/2}} + e \operatorname{erf} \frac{\lambda}{2v^{1/2}} + f \qquad (73)$$

where:-

$$a = \frac{1}{2D} \left[D_{BC} \, (C_C^{+} - C_C^{-}) - [(D_{CC} - D_{BB}) - D] \cdot \frac{(C_B^{+} - C_B^{-})}{2} \right]$$

$$b = \frac{1}{2} \, (C_B{}^{+} - C_B{}^{-} - 2a)$$

$$c = \frac{1}{2} \, (C_B{}^{+} + C_B{}^{-})$$

$$d = \frac{1}{2D} \left[D_{CB} \, (C_B^{+} - C_B^{-}) - [(D_{BB} - D_{CC}) - D] \cdot \frac{(C_C{}^{+} - C_C{}^{-})}{2} \right]$$

$$e = \frac{1}{2} \, (C_C{}^{+} - C_C{}^{-} - 2d)$$

$$f = \frac{1}{2} \, (C_C{}^{+} + C_C{}^{-})$$

$$u = D_{BB} + \frac{1}{2} \, [(D_{CC} - D_{BB}) + D]$$

$$v = D_{CC} + \frac{1}{2} \, [(D_{BB} - D_{CC}) - D]$$

$$D = [(D_{BB} - D_{CC})^2 + 4D_{BC}D_{CB}]^{1/2}$$

This solution is very complex in the general case, but the solutions are simplified considerably if one of the cross-coefficients is zero. Also in the special case in which $D_{BB} = D_{CC}$ while $D_{CB} = 0$, D (defined above) goes to zero, so that a and d (and hence b and e) become indeterminate. However, use of L'Hôpital's rule yields a solution.

The assumption of finite constant values for the cross coefficients of a ternary system can lead to the prediction of negative concentrations near the binary limits of a ternary isotherm. Therefore, such assumptions are clearly unreasonable, but Kirkaldy [65] has expressed the opinion that provided the overall change in composition across a diffusion couple is no more than 20% of the average composition, then the assumption of constant coefficients is justified. However, many practical situations fall outside the scope of this limitation and so solutions to the diffusion equation must be sought without the assumption of constant coefficients. Again, attention will be focussed on a ternary system:-

(b) Solutions with Variable Coefficients

For a ternary system with independently variable coefficients, equation (69) becomes:-

$$\frac{\partial C_B}{\partial t} = \frac{\partial}{\partial x}\left[D_{BB}\ \frac{\partial C_B}{\partial x}\right] + \frac{\partial}{\partial x}\left[D_{BC}\ \frac{\partial C_c}{\partial x}\right] \qquad (74)$$

$$\frac{\partial C_c}{\partial t} = \frac{\partial}{\partial x} D_{CB} \frac{\partial C_B}{\partial x} + \frac{\partial}{\partial x} D_{CC} \frac{\partial C_C}{\partial x} \qquad (75)$$

Such equations may be solved directly by numerical methods [67]. However, an integral iterative technique has been developed by Kirkaldy, Lane and Mason [42] which is claimed to be less tedious than direct numerical solution since the convergence of the iteration process is very rapid provided the diffusion coefficients vary only moderately with composition. Nevertheless, this solution remains complex and unwieldy. Simplification can only be achieved by seeking dependences amongst the coefficients which necessitates a return to thermodynamics, i.e. the resultant equations will involve chemical potentials.

This situation demands some relationship between chemical potential and composition which can be applied to solutions showing neither Henrian nor Raoultian behaviour. Wagner [68] has shown that for a multicomponent solution comprising A as solvent and dilute with respect to the solutes B, C, D etc., the logarithm of the activity coefficient (γ) of one of the solutes (i) is given by:-

$$\ln \gamma_i = \ln \gamma_i^o + N_B \, \varepsilon_{iB} + N_C \, \varepsilon_{iC} + N_D \, \varepsilon_{iD} \text{ etc.} \qquad (76)$$

Where,

γ_i^o = Activity Coefficient of i at infinite dilution, i.e. the Henrian Activity Coefficient.

N_j = Mole fraction of component j.

ε_{ij} = Interaction Parameter defined as follows:-

$$\varepsilon_{ij} = \left. \frac{\partial \ln \gamma_i}{\partial N_j} \right|_{N_A \to 1} \qquad (77)$$

Bolze, Coates and Kirkaldy [69] have utilized this, so called, Wagner Dilute Solution Model (equation (76)) to derive dependencies amongst the diffusion coefficients of a ternary system. They assumed a vacancy diffusion model and commenced their analysis with a fundamental diffusion equation written in terms of chemical potential rather than concentration gradients. The application of thermodynamic and kinetic constraints enabled them to produce expressions for and relationships between the fundamental coefficients. As was shown earlier (equations (62) and (63)), fundamental coefficients can be replaced by practical coefficients (which relate fluxes to concentration rather than chemical potential gradients), but the translation between the two involves the derivatives of chemical potential with respect to composition. However, such derivatives can easily be obtained if the Wagner Dilute Solution Model can be invoked. Thus, Bolze, Coates and Kirkaldy were able to transform the equations describing the fundamental coefficients into expressions for the practical coefficients with the aid of equation (76).

The following are the expressions they obtained for the two direct coefficients to the first order in concentrations:-

$$D_{BB} = a^2 P_B \left[1 + \frac{C_B}{\rho A} \left(\varepsilon_{BB} - \frac{\bar{V}_B}{\bar{\bar{V}}_A} + \frac{P_A}{P_B} \right) + \ldots . \right] \qquad (78)$$

$$D_{CC} = a^2 P_C \left[1 + \frac{C_C}{\rho_A} \left(\varepsilon_{CC} - \frac{\bar{V}_C}{\bar{V}_A} + \frac{P_A}{P_C} \right) + \ldots . \right] \qquad (79)$$

Where,

a = Lattice Parameter

P_i = Jump Frequency of i atoms in the x direction

ρ_A = Molar Density of Solvent A

$\bar{V}_i$ = Partial Molar Volume of i

ε_{ij} = Wagner Interaction Parameter

It is seen from equations (78) and (79) that in the dilute limit (C_B and $C_C \to 0$) the two direct coefficients approach constancy. Further, throughout the dilute range, these coefficients remain slowly varying functions of composition so that the assumption of average constant values for D_{BB} and D_{CC} is not unreasonable.

The other results obtained by Bolze, Coates and Kirkaldy are expressions for the ratios of the cross coefficients to the respective direct coefficient:-

$$\frac{D_{BC}}{D_{BB}} = \frac{C_B}{\rho A} \left[\varepsilon_{Bc} - \frac{\bar{V}_C}{\bar{V}_A} \cdot \frac{P_C}{P_B} + \frac{P_A}{P_B} - \varepsilon_{BB} + \frac{\bar{V}_B}{\bar{V}_A} \cdot \varepsilon_{Bc} - \frac{\bar{V}_C}{\bar{V}_A} \cdot \frac{P_C}{P_B} + \frac{P_A}{P_B} \cdot \frac{C_B}{\rho A^2} \right.$$

$$\left. + \quad \varepsilon_{CC} + \frac{\bar{V}_C}{\bar{V}_A} \cdot - \frac{\bar{V}_B}{\bar{V}_A} - \frac{\bar{V}_C}{\bar{V}_A} \cdot \frac{P_C}{P_B} + \frac{P_A}{P_B} \cdot \frac{C_C}{\rho A^2} + \ldots\ldots . \right]$$

To the first order in concentration this becomes:-

$$\frac{D_{BC}}{D_{BB}} = \frac{C_B}{\rho A}\left[\varepsilon_{BC} - \frac{\bar{V}_C}{\bar{V}_A} \cdot \frac{P_C}{P_B} + \frac{P_A}{P_B}\right]$$

- which for dilute solutions can be written:-

$$\frac{D_{BC}}{D_{BB}} = \alpha_{BC}\, C_B \qquad (80)$$

Similarly:

$$\frac{D_{CB}}{D_{CC}} = \alpha_{CB}\, C_C \qquad (81)$$

Where α_{BC} and α_{CB} are Proportionality Constants.

If $P_A = P_B = P_C$ and $\bar{V}_A = \bar{V}_B = \bar{V}_C$ (i.e. when molar volumes are identical and the Kirkendall Effect vanishes) then α_{BC} and α_{CB} become purely thermodynamic and equations (80) and (81) become:-

$$\frac{D_{BC}}{D_{BB}} = \varepsilon_{BC} N_B \qquad (82)$$

$$\frac{D_{CB}}{D_{CC}} = \varepsilon_{CB} N_C \qquad (83)$$

Where N_B and N_C are Mole Fractions.

It is of interest to note that Wagner showed ε_{BC} to be equal to ε_{CB} in the dilute limit.

Coupled with the results obtained earlier for the direct coefficients, equations (80) and (81) can be approximated to $D_{BC} \propto C_B$ and $D_{CB} \propto C_C$ in the dilute range. Such a result is reasonable in that it predicts that D_{BC} will go to zero when C_B goes to zero (and similarly for D_{CB} and C_C):-

From equation (65)

$$J_B = - D_{BB} \frac{\partial C_B}{\partial x} - D_{BC} \frac{\partial C_C}{\partial x}$$

When C_B goes to zero, $\partial C_B/\partial x$ and J_B go to zero, and therefore so must D_{BC} because $\partial C_C/\partial x$ may remain finite.

With the aid of equations (80) and (81) together with the assumption of average constants for the values of the direct coefficients, the solutions of equations (74) and (75) are substantially simplified.

Consider equation (74), substituting for D_{Bc} from equation (81):-

$$\frac{\partial C_B}{\partial t} = D_{BB} \cdot \frac{\partial^2 C_B}{\partial x^2} + D_{BB}\, \alpha_{BC}\, C_B \cdot \frac{\partial^2 C_C}{\partial x^2} + D_{BB}\, \alpha_{BC} \cdot \frac{\partial C_B}{\partial x} \cdot \frac{\partial C_C}{\partial x} \qquad (84)$$

Solution of equation (84) requires knowledge of the analytical solution for CC, but the diffusion equation for component C (equation (75)) can only be solved knowing the expression for C_B (i.e. the solution of equation (84)). Therefore, the assumption is made that in calculating the concentration distribution of a given component (B say) in a dilute solution, the neglect of the cross diffusional effects on the other component (C) is justified. i.e. For the purposes of solving equation (84), D_{CB} is assumed to be zero, so that equation (75) becomes:-

$$\frac{\partial C_C}{\partial t} = D_{CC} \frac{\partial^2 C_C}{\partial x^2} \tag{85}$$

- which has a simple error function solution.

Similarly, the solution for C_C is obtained by setting D_{BC} to zero. This procedure permits the solution to equations (74) and (75) to be obtained by a straightforward finite difference technique.

4.4 Determination of Diffusion Coefficients for a ternary system

From what has already been said, it would be inappropriate to start with the assumption of constant coefficients when considering the means of determining such coefficients in a general ternary system. Therefore, by analogy with the procedure adopted for determining variable coefficients in binary systems, consideration is given to an extension of the Boltzmann-Matano technique which would be amenable to a three component system.

Kirkaldy [70] has observed that equation (69) written in terms of $\lambda(= x/t^{1/2})$ can be integrated to give:-

$$\int_{C_i^-}^{C_i} \lambda dCi = -2 \sum_{j=1}^{n-1} Dij \cdot \frac{dCj}{d\lambda} \bigg|_{C_i = C_i} \qquad i = 1 \text{ to } n-1 \tag{86}$$

Since the concentration profiles to be analysed are at a fixed time, equation (86) can be written:-

$$\int_{Ci^-}^{C_i} xdC_i = -2t \sum_{j=1}^{n-1} Dij \left.\frac{dCj}{dx}\right|_{C_i=C_i} \qquad i = 1 \text{ to } n-1 \qquad (87)$$

If n = 2, equation (87) reduces to equation (23) which is the basis for the Boltzmann-Matano method of determining diffusion coefficients in binary systems. As described earlier, D can be determined at any composition point across a binary diffusion couple by measuring the integral $\int_{C^-}^{C} x.dC$ and gradient dC/dx at the composition point of interest from an experimentally determined concentration profile, followed by substitution in equation (23). For a multicomponent system, however, things are not so simple. It is seen from equation (87) that for an n component system there are (n-1) equations available for the determination of $(n-1)^2$ coefficients. Thus when n exceeds two, it becomes impossible to determine the coefficients from the measured concentration profiles across a single diffusion couple.

Consider a ternary system, for which there exists four interdiffusion coefficients and two equations of the form (87). Further, consider two different diffusion couples in this system which have a common composition point. At that common composition the values of the four coefficients in one couple should be the same as those of the respective coefficients in the other. Therefore, the equations appropriate to each couple can be taken as a common set and can be solved simultaneously to give the values of the four coefficients at the common composition point. It is comparatively easy to design a pair of couples to have a common composition point since the latter coincides with the intersection of the diffusion paths of the two couples. (A diffusion path is a graph showing the variation of composition across a ternary diffusion couple without containing any spatial information.)

It is apparent that there is a substantial drop in the productivity of diffusion measurements in going from a binary to a ternary system. For a binary system, the value of the single interdiffusion coefficient can be determined over a range of compositions from a single couple, while for a ternary system, two carefully chosen couples are required in order to determine the interdiffusion coefficient matrix at a single composition point. For systems of more than three components, it is likely that the amount of experimentation and computation required to determine diffusion coefficients by this technique would be prohibitive unless approximations are made.

At this point mention may be made of a radical approach to the description of diffusion in multicomponent systems by De Hoff, Anusavice and Wan [71,72]. They have considered diffusion in ternary systems and have swept aside the traditional matrix of interdiffusion coefficients in favour of a simpler and more direct approach. The components of a ternary system are given Relative Penetration Tendencies which relate the diffusion rate of any given species to those of the other two. This is an approximate approach, but is shown to result in predictions in close agreement with observation for a number of ternary systems. It may be that for dealing with systems of more than three components, a scheme similar to that described above will be the only practicable theoretical description of diffusion.

Returning to equation (87), it is seen that measurement of the integral term in the equation requires knowledge of the absolute value of x at any point on the profile. This means that the origin for making measurements of x must be known. This origin is the Matano Interface which is defined by writing equation (87) at $Ci = Ci^+$ $(x=\infty)$ where all concentration gradients are zero:-

$$\int_{C_i}^{C_i^+} x.dC_i = 0 \tag{88}$$

The location of the Matano Interface is a tedious and often inaccurate procedure. Further, if the molar volume varies with composition, then the Matano Interfaces defined for each species will not coincide, which adds further to the workload. Therefore, following the transformation of equation (23) into equation (26) [44,45,46], which obviated the need to locate the Matano Interface when carrying out a Boltzmann-Matano analysis of a binary system, Whittle and Green [73] deduced the following equation, which represents a similar transformation for the multicomponent case:-

$$(C_i^+ - C_i^-) \left[(1-Y_i) \int_{-\infty}^{x} Y_i \, dx + Yi \int_{x}^{+\infty} (1-Y_i) dx \right] =$$

$$2t \sum_{j=1}^{n-1} Dij \cdot \frac{dCj}{dx} \tag{89}$$

$$i = 1 \text{ to } (n-1)$$

Where : $$Yi = \frac{C_i - C_i^-}{C_i^+ - C_i^-} \qquad (90)$$

4.5 Analysis of Concentration Profiles Exhibiting Maxima and Minima

The situation can often arise in multicomponent diffusion couples, particularly when diffusional interaction is strong, where the concentration of one or more of the components exhibits a maximum (or minimum) and the local value of C_i lies outside the range C_i^- to C_i^+. Under these circumstances, x is not a single-valued function of C_i over part of the concentration profile, and, within this range, the integrals in equations (87) and (88) cannot be evaluated. This has serious implications for the analysis of concentration profiles in multicomponent systems, but appears not to have been recognized by previous workers (see for example [74,75,76]). It is not possible to assess the magnitude of the errors which might have been introduced, however, since details of the actual integration procedures have not been published.

A complete presentation of the mathematical treatment of a generalized concentration profile with m turning points (maxima and minima), from which it is desired to know the diffusion coefficient matrix at some concentration C_i lying between the p^{th} and $(p+1)^{th}$ turning points, is given in [77].

Briefly, it is necessary to separate the profile into (m+1) parts, for each of which x is a single-valued function of C_i. A separate integral of the type $\int x.dC_i$ can then be defined for each part of the profile and used in an expanded version of equation (87). Integration by parts is then used to convert all the integrals to the type $\int C_i \cdot dx$ and, in this format, the separate integrals can be recombined since C_i is a single-valued function of x throughout the entire profile:-

$$x.Z_i - \int_{-\infty}^{x} Z_i.dx = -2t \sum_{j=1}^{n-1} D_{ij} \frac{dZ_j}{dx} , \tag{91}$$

Where, $Z_i = C_i - C_i^-$, and has been introduced to produce a finite integral.

The term x in equation (91) must be measured from the Matano Interface. Using the technique of den Broeder [45], however, equation (91) can be modified so that the distance parameter only appears in differential form, thus obviating the need to locate the Matano Interface. The result of this procedure turns out to be none other than equation (89), which can be modified to account for changes in molar volume (V_m) as follows [45,73]:-

$$(C_i^+ - C_i^-) \left[(1-Y_i) \int_{-\infty}^{x} \frac{Y_i}{V_m} \cdot dx + Y_i \int_{x}^{+\infty} \frac{(1-Y_i)}{V_m} \cdot dx \right] = 2t. \sum_{j=1}^{n-1} \frac{D_{ij}}{V_m} \frac{dC_j}{dx} \tag{92}$$

In general, V_m can be approximated to a linear function of composition.

There is an added advantage of analysing concentration profiles containing maxima or minima, since at those points, the gradient dC_i/dx of one of the components is zero. Thus, the right hand side of equation (89) can be modified. For example, at a turning point in the C profile of the ternary system ABC with A as solvent:-

$$(C_B^+ - C_B^-)\left[(1-Y_B)\int_{-\infty}^{x} Y_B \cdot dx + Y_B \int_{x}^{+\infty} (1-Y_B)\cdot dx\right] = 2t\cdot\left[D_{BB}\,\frac{dC_B}{dx} + 0\right] \qquad (93)$$

$$(C_C^+ - C_C^-)\left[(1-Y_C)\int_{-\infty}^{x} Y_C \cdot dx + Y_C \int_{x}^{+\infty} (1-Y_C)\cdot dx\right] = 2t\cdot\left[D_{CB}\,\frac{dC_B}{dx} + 0\right] \qquad (94)$$

and thus D_{BB} and D_{CB} can be calculated directly without the requirement of having two diffusion paths crossing at a common composition [75].

A common design of diffusion couples in ternary diffusion studies, is the so-called Darken couple, in which the end concentrations of one of the components (e.g. B) are identical, while the other component (C) has a step change at the original interface. This type of couple is useful in demonstrating the existence of diffusional cross effects [53]. However, as $C_B^- = C_B^+$, then Y_B as defined by equation (90) is now indeterminate. Equation (91) has now to be used as it stands, with x being measured from the Matano interface. Under these conditions, the location of the Matano interface is trivial, since it is the position where the profile cuts the $C_B = C_B^- = C_B^+$ line.

6. CONCLUDING REMARKS

At the beginning of this review, it was emphasized that an understanding of multicomponent diffusion was important with respect to many of the changes of structure and chemical composition occurring in metals. It is hoped that this review may help to provide such an understanding, dealing as it does with the complete evolution of ideas on diffusion theory from Adolf Fick to the present day. It has been shown how diffusion coefficient data may be determined for ternary systems by the analysis of concentration profiles across infinite diffusion couples and it is hoped that these techniques will be fully implemented in the future for the generation of diffusion data for ternary systems to complement the already bountiful data referring to binaries.

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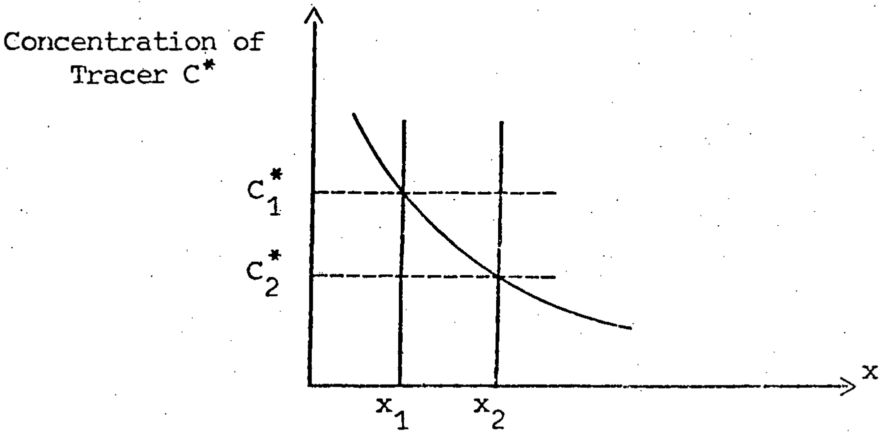

Figure 1

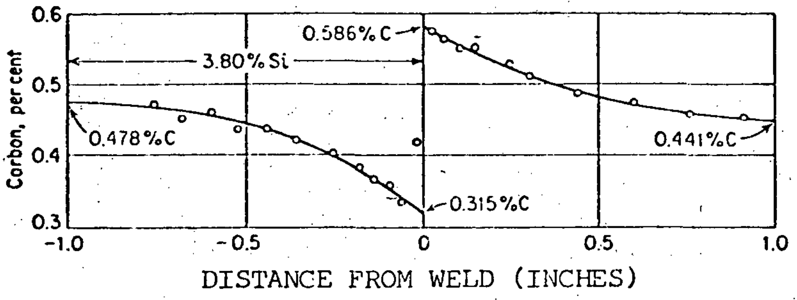

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Figure 2

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